STABLE CARBON ISOTOPE RATIO OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN THE ENVIRONMENT: VALIDATION OF ISOLATION AND STABLE CARBON ISOTOPE ANALYSIS METHODS

A Dissertation

by

MOON KOO KIM

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2004

Major Subject: Oceanography

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Approved as to style and content by:

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ABSTRACT

Stable Carbon Isotope Ratio of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment: Validation of Isolation and Stable Carbon Isotope Analysis Methods.

(August 2004)

Moon Koo Kim, B.S., Inha University, Korea;

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous, toxic contaminants that are released to the environment from various petrogenic and pyrogenic sources. In an effort to more clearly identify and trace sources of PAHs in the environment, purification and compound specific isotope analysis methods were developed to accurately measure the stable carbon isotope ratio of individual PAHs. Development of the method included improving accuracy and precision of the isotopic measurement by producing highly pure extracts using various chromatographic techniques. The method was refined by improving compound separations using purification techniques and high resolution chromatographic columns. The purification method consists of alumina/silica gel column chromatography, gel permeation chromatography and thin layer chromatography. The mean recovery of PAHs after the purification procedure was approximately 80 %. Sample purities after purification were verified by GC/FID and full scan mass spectrometry. To better resolve peaks and provide more accurate stable carbon isotope measurements, various gas chromatographic conditions were evaluated. The precision of the method ranged between 0.08 and 0.43 ‰. The analytical protocols were evaluated to confirm compositional and stable isotopic integrity during purification and stable isotopic analysis. To confirm the utility of the purification and isotope analysis methods, various environmental samples from marine, land and lacustrine environments were analyzed. The isolates were analyzed for the composition and the stable carbon isotope ratios of PAHs. The stable carbon isotope ratio was measured by GC/IRMS and the

results, along with quantitative compound compositions, were used to characterize and identify the contaminant sources. The sources of the PAHs in the study areas were differentiated by PAH molecular ratios and confirmed by stable carbon isotope ratios. This study confirms that compound specific isotope analysis of pollutants by GC/IRMS can be used to identify PAH sources in environmental samples. The study also confirms that the purification and stable carbon isotope analysis methods that were developed can be used to accurately measure the stable carbon isotope ratios of PAHs in environmental samples for the purpose of source identification. GC/IRMS measurement of stable isotopic compositions can be an effective fingerprinting method when used in conjunction with traditional molecular composition methods.

DEDICATION

To my parents, my wife Sunhwa, my daughters Benita and Janice, and brother Nakhyun.
Thank you for your patience, support and prayers. I love you.

ACKNOWLEDGMENTS

I thank God for always being with me and for everything He has done for me.

I would like to express my special appreciation to my advisor, Dr. Mahlon C. Kennicutt II, for his encouragement, guidance and support during my Ph.D. study at Texas A&M University. I'm also very grateful to Dr. Yaorong Qian, Dr. Luis A. Cifuentes, and Dr. Kirby C. Donnelly, as members of my committee, for their valuable assistance and suggestions. Dr. Qian has taken care of me and guided my research from the very beginning of my graduate study. Dr. Cifuentes let me use his laboratory and instruments including GC/IRMS. Dr. Donnelly provided me with his precious samples.

I also wish to thank Dr. Terry L. Wade, Dr. Jose L. Sericano, and Dr. Stephen Sweet for their valuable assistance and suggestions during my work at the Geochemical and Environmental Research Group. I would also like to thank Dr. Assem O. Barakat at Alexandria University, Egypt, for letting me participate in his precious research during my graduate study. Special thanks go to Mr. Brian Jones, Mr. Carlton Rauschenberg, and Dr. Gregory G. Salata for their significant help in learning and using GC/IRMS in the laboratory of Dr. Cifuentes. I also thank Dr. Hyun-Min Hwang and Dr. June-Soo Park for their precious help and guidance. Thanks to all current and former GERG staff, including Alvin, Andrew, Blake, Carolyn, Cindy, Debbie, Debz, Gary, George, James, Javier, Lisa, Marty, Mary, Paul, who gave me a lot of help during my study at Texas A&M. I also give special thanks to my good friends, Young Baek and Seong Ho, for their continuing support.

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CHAPTER I

INTRODUCTION

Organic pollutants are an ever increasing concern as a stressor of ecosystems and an agent of degradation of the condition and health of natural resources. Many classes of industrial and combustion-derived chemicals are released to and persist in the environment including polycyclic aromatic hydrocarbons (PAHs) and halogenated aromatics (HAs) such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxin (PCDDs), polychlorinated dibenzofurans (PCDFs), and organochlorine (OC) insecticides. PAHs are hydrocarbons that contain at least two fused benzene rings. PAHs are known as one of the largest and most structurally diverse class of chemical compounds. PAHs are environmental contaminants that are detected almost everywhere in the world, including water, sediment/soil, air, and organisms (Harvey, 1997). PAHs can be formed by either thermal alteration of buried organic matter or incomplete combustion of organic matter (Suess, 1976; Sims and Overcash, 1983; Nikolaou *et al*., 1984). PAHs are introduced into the environment by a variety of mechanisms. Extensive use of fossil fuels and biomass burning are major sources of petrogenic and pyrogenic PAHs in the environment (Yanik *et al*., 2003). Because of their high hydrophobicity, PAHs strongly partition into sediments and/or biological tissues (Wilson and Jones, 1993; Roper *et al*., 1997). The hydrophobicity and low volatility of high molecular weight PAH contribute to their environmental persistence. PAHs have long been suspected carcinogens and mutagens. PAHs in some fossil fuel products, such as benzo(*a*)pyrene, are known to cause cancer, skin disease and hormone malfunction (Dipple, 1985; ATSDR, 1995). The widespread occurrence of PAHs in the environment, along with their persistence and harmful toxic properties, has prompted extensive research into the fate and effects of PAHs in the environment. Most of the research is

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This dissertation follows the style and format of the Marine Pollution Bulletin.

aimed at characterizing the distribution of anthropogenic PAHs and their degradation products in environmental matrices. Relatively few studies have used compound specific isotope analysis to define PAH sources.

Integrated assessments of the environmental effects of pollutants document not only the chemical and toxic nature of the contaminants, but also their sources and the routes by which they are transmitted through natural systems. With this information, remediation of contaminated sites and future contamination prevention is possible. One approach to identify the sources of contaminants is by relating concentration gradients to possible point sources. Another approach is to measure the concentrations of contaminants relative to one another and use compositional information as a "fingerprint". However, concentration alone in various matrices is often inadequate to provide information on the contaminant's origin. Contaminants generally result from multiple sources and are subject to complex natural alteration processes. After contaminants are released to the environment, they can be transported in a variety of ways ending up sequestered in sediment/soil, water and/or biological tissues. Non-point sources complicate the linkages between identifiable inputs and observed environmental concentrations. Contaminants can also be subject to significant modification by microbiological processes once released to the environment. Multiple inputs and the chemical and biological alterations of contaminants often change the original composition of contaminants preventing a clear resolution of contaminant sources, impacts, and fate (O'Malley *et al*., 1994).

Intrinsic tracers, whose properties do not change with concentration change, such as stable carbon isotope ratio, are one approach that may resolve complex contaminant chemistries and fates. Contaminants are produced from various industrial, natural, and synthetic processes. Chemicals produced from different sources by fundamentally different processes or raw materials may exhibit unique stable isotopic compositions which could be used as a method to identify sources. Compound specific isotope analysis (CSIA) of pollutants by gas chromatography linked with an isotope ratio mass spectrometer (GC/IRMS) has the potential to identify contaminant sources and to trace

their transfer through natural systems. GC/IRMS measurements of stable isotopic compositions for the purpose of tracing contaminants may be an adjunct to traditional molecular methods. Several researchers have performed compound specific isotope analysis of PAHs (O'Malley *et al*., 1994; Ballentine *et al*., 1996; O'Malley *et al*., 1996; O'Malley *et al*., 1997; McRae *et al*., 1999; Norman *et al*., 1999; McRae *et al*., 2000) but the methods used for purification and compound specific isotope analysis were not completely validated. The stable isotopic composition of bulk organic matter is a weighted average of the isotopic compositions of hundreds or even thousands of individual chemical components, each having its own isotopic abundances. To trace the source and history of organic materials, isolation of individual molecular components using various chromatographic techniques is needed. Separation techniques must provide sufficient material for precise and accurate stable isotope analysis. The more pure the analyte introduced into the GC, the less the interferences from co-elution, peak overlap, and unresolved complex mixture (UCM) bleed. In order for compound specific isotope analysis to be used for source identification, the extract must be purified to avoid interferences and stable isotopic integrity must be preserved throughout the purification procedure.

The objective of this study was to develop a purification and isotope analysis method to more accurately measure the stable carbon isotope ratios of PAHs for defining the sources and fate of pollutants in the environment. Development of the methods included improving the accuracy and precision of the isotopic measurement by removing interference from co-eluting compounds or unresolved complex mixtures by producing highly purified samples using chromatographic techniques. The method was refined by improving compound separations using purification techniques and high resolution chromatographic column. Purification techniques for isotope analysis were developed and method accuracy and precision were verified with authentic standards. The purity of isolates was also verified by gas chromatography with flame ionization detection and mass spectrometry. The analytical protocols were evaluated to ensure that compositional

and stable isotopic integrity was preserved by processing authentic standards of known stable isotopic composition through the analytical protocol.

The second objective was to use the purification and isotope analysis methods to analyze various environmental samples to confirm the utility of the method as a source identification tool. Soils and sediments from marine, lacustrine and land environments were tested. The study also included the characterization of contaminant sources using PAH compositional data. To accurately measure the stable carbon isotope ratio of individual PAH compounds, sample extracts were purified using purification method involving various chromatographic and high performance liquid chromatographic techniques. The isolates were analyzed for PAH content and stable carbon isotope ratios of individual compound. Stable carbon isotope ratios and quantitative compound distributions were used to trace and identify the source of the detected contaminants. The stable isotopic compositions of contaminants from various locations were measured. Traditional methods to identify contaminant sources using compositional information were compared with stable carbon isotopic signatures as source identifiers.

CHAPTER II

BACKGROUND

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons that contain at least two fused benzene rings in linear, angular, or cluster arrangements (Fig. 2.1). PAHs in the molecular weight range between naphthalene (128.16) and coronene (300.36) are of environmental concern (Ashok and Saxena, 1995). Many PAHs are stable and persistent in the environment and toxic. PAHs are common byproducts formed either by thermal alteration of buried organic matter (petrogenic) or by incomplete combustion of organic matter (pyrogenic) (Suess, 1976; Sims and Overcash, 1983; Nikolaou *et al*., 1984). PAHs also exhibit extraordinary structural diversity. The number of possible PAH isomer is large and it expands rapidly as the number of rings and alkylations increase (Table 2.1). However, not all the possible PAHs exist because of the low conformational stability of larger ring numbers, especially for linearly fused PAHs (Harvey, 1997).

Most complex PAHs are named by the IUPAC system of nomenclature. PAH compound with complex ring systems use the name of the base component rings and adds the name of the attached ring system as a prefix. When adding the name of the attached component to the base component, the attached component ending of "-ene" is changed to "-eno" and the final "o" of the prefix is omitted if the name of the base component starts with vowel. All PAHs have the maximum number of conjugated double bonds and this is why PAHs are denoted by the ending "-ene". The numbers on the ring indicate carbon positions where alkyl groups can be substituted. In order to number the ring positions, the PAH is oriented so that the maximum number of rings lies in a horizon and as many rings as possible are at the upper and right section of the compound. Numbering starts with the carbon atom in the uppermost counterclockwise position on the ring the farthest to the right. It proceeds in a clockwise direction and omits atoms at ring junctures. The exception to the numbering rule is for anthracene and phenanthrene, which retain an historical numbering system (Fig. 2.1). Isomers are

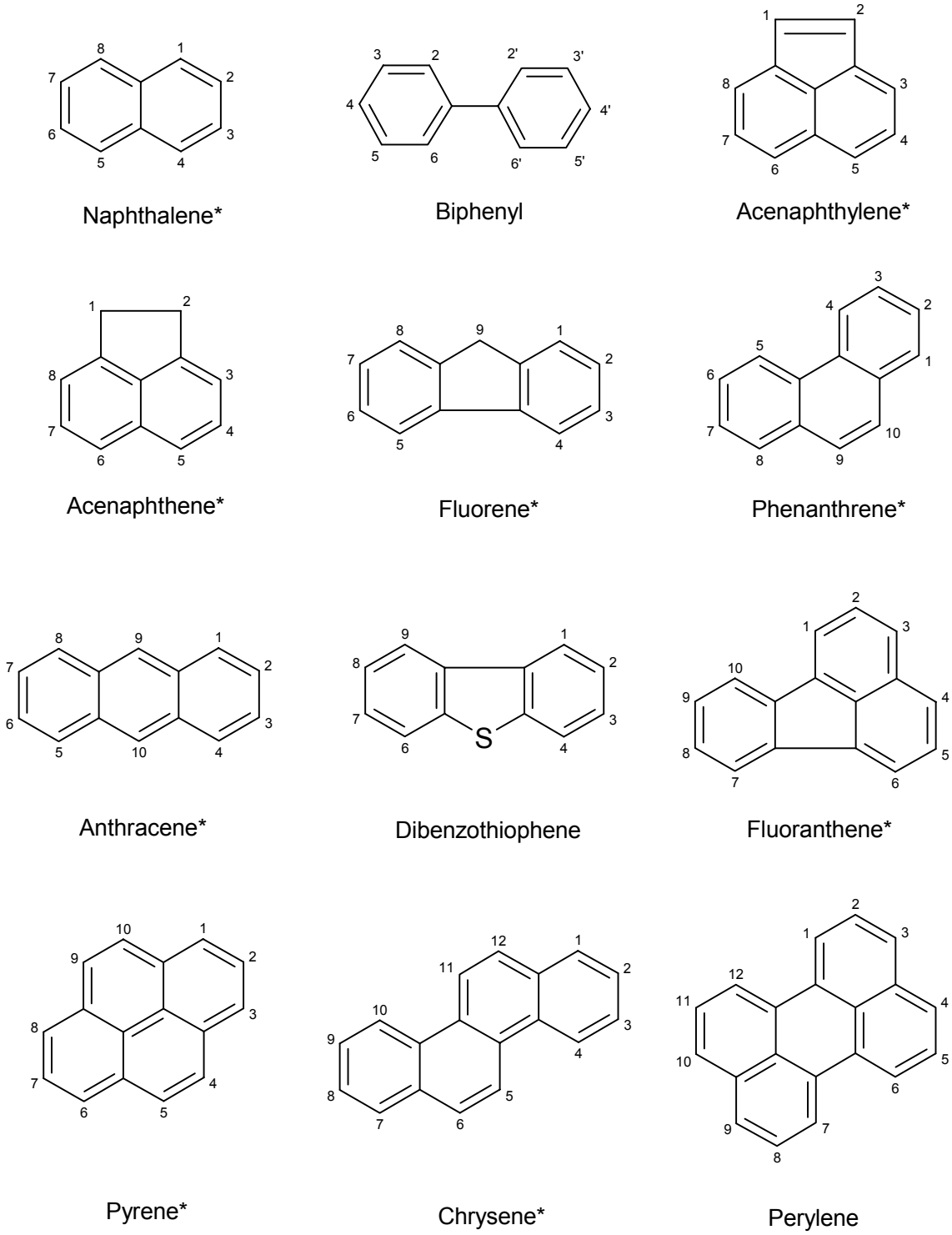
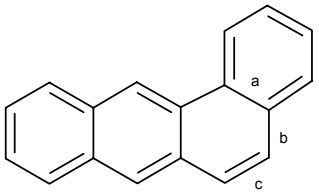
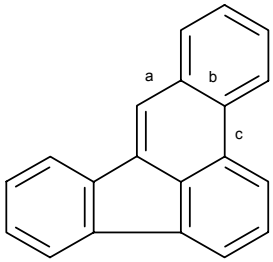


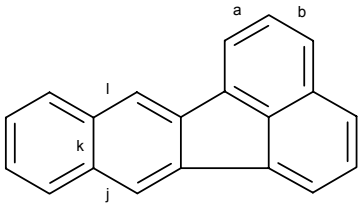
Fig. 2.1. Chemical structures of PAHs. 16 EPA priority PAHs are marked with an asterisk.



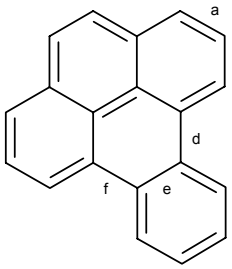
Benz[a]anthracene*



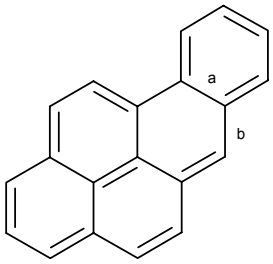
Benzo[b]fluoranthene*



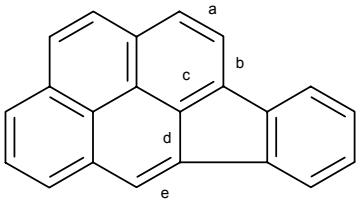
Benzo[k]fluoranthene*



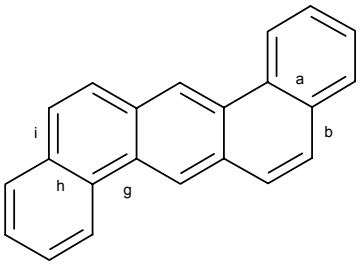
Benzo[e]pyrene



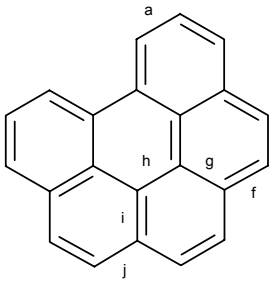
Benzo[a]pyrene*



Indeno[1,2,3-cd]pyrene*



Dibenz[a,h]anthracene*



Benzo[ghi]perylene*

Fig. 2.1. Continued.

Table 2.1.
The number of possible PAH isomers.*

Formula	Number of rings	Theoretical isomers	Isomers reported
$C_{10}H_8 - C_{22}H_{14}$	2 – 5	20	20
$C_{26}H_{16}$	6	37	27
$C_{30}H_{18}$	7	123	23
$C_{34}H_{20}$	8	> 411	8
$C_{38}H_{22}$	9	> 1,489	66
$C_{42}H_{24}$	10	> 5,572	7
$C_{46}H_{26} - C_{58}H_{34}$	11 – 14	> 1,600,000	7

* Data are from Harvey (1997).

distinguished by lettering the peripheral sides of the base ring system, which has an attached ring system. It begins with “a” for the side “1-2”, “b” for the side “2-3”, etc. The name of partially hydrogenated derivatives use an appropriate prefix like “dihydro-“, “tetrahydro-“, appended to the name of the parent PAHs (Loening *et al*., 1990; Harvey, 1991; Harvey, 1997).

Sources of PAHs

Extensive use of fossil fuels and biomass burning are the major sources of anthropogenic PAHs in the environment (Yanik *et al*., 2003). Major sources of petrogenic PAHs also include crude oil and its refined products, coal, and oil shale (Harvey, 1997; Page *et al*., 1999). Petrogenic PAHs are derived from uncombusted petroleum products and contain relatively low molecular weight PAHs with one to three rings (Neff, 1979). They are characterized by homologous families of related PAHs such as, naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes, where the alkylated PAHs for each family far exceed the unsubstituted parent PAHs (Lee *et al*., 1981; Page *et al*., 1999). The content of PAHs in petroleum crude oil is about 1% by weight and 5~20% in crude oil obtained from coal (Bence *et al*., 1996; Pickering, 1999). Oil seepage is a natural source of petrogenic PAHs in the marine environment (Kvenvolden and Harbough, 1983; Anderson *et al*., 1983; Kennicutt *et al*., 1987; Kennicutt *et al*., 1988; Kennicutt *et al*., 1989; Kennicutt and Brooks, 1990). Pyrogenic PAHs are generated by the combustion of fossil fuels and organic matter. During pyrolysis and pyrosynthesis, cracking of complex organic molecules into smaller and unstable fragments (pyrolysis) results in the formation of free radicals with short average lifetimes. The highly reactive free radicals produce more stable and highly condensed aromatic ring systems through recombination reactions (pyrosynthesis) (Ballentine *et al*., 1996; Mastral and Callen, 2000). The extent and type of PAH production during pyrolytic reactions depends on the combustion temperature and mixing conditions in the flame (Blumer, 1976; Ramdahl *et al*., 1982; Colmsjo *et al*., 1986). At high temperatures under anaerobic conditions, relatively simple mixtures of unsubstituted PAHs are

produced. PAHs produced at high temperatures also show increased levels of high molecular weight compounds, and the dominant isomers are those that form most rapidly, i.e., the kinetically favored isomers (Simpson *et al*., 1996). At intermediate temperatures, the products consist of complex mixtures of alkyl-substituted and unsubstituted PAHs. At lower temperatures, the predominant products are alkyl-substituted PAHs, and when several isomeric PAHs are possible, the isomers with higher thermodynamic stability are favored (Simpson *et al*., 1996). Alkylation of PAHs increases with decreasing combustion temperature, so that the higher the temperature, the more parent PAHs are produced (Hites *et al*., 1980A; Harvey, 1997). For example, crude oils formed at relatively low temperature, exhibit characteristic patterns of aromatic hydrocarbon components where alkyl-substituted PAHs far exceed the unsubstituted PAH components (Blumer, 1976; NRC, 1983; Masclet *et al*., 1987). The absolute amount of PAHs generated during incomplete combustion is also strongly dependent on combustion temperature (Wang *et al*., 1999). Pyrogenic sources produce PAH distributions dominated by the parent compounds with 3-, 4-, and 5-ring PAHs. Fluoranthene and pyrene are usually considered to be the major compounds in combustion derived PAH mixtures (Page *et al*., 1999; Witt and Trost, 1999). Some pyrogenic PAHs can also result from natural processes such as volcanic activity and forest fires. Rapid formation of retene occurs during the combustion of pinewood (Ramdahl, 1983). However, the major sources of PAHs to the environment are industrial activities including coal coking; production of carbon black, creosote, and coal tar; petroleum refining; synthetic fuel production from coal; waste incineration; and use of internal combustion engines (NRC, 1983; Baek *et al*., 1991).

Distribution of PAHs in the Environment

PAHs are common environmental contaminants and are found in considerable amounts in air, water, sediment/soil, and organisms (Harvey, 1997). The most abundant individual PAHs include fluoranthene, pyrene, chrysene, benzo(*b*)fluoranthene, benzo(*j*)fluoranthene, and benzo(*k*)fluoranthene (Jones *et al*., 1989; Berset and Holzer,

1995). PAHs in the atmosphere are derived mainly from the combustion of fossil fuels for heat and power generation, anthropogenic burning, evaporation of petroleum, and vehicle emissions. Fossil fuel burning for motor vehicle operation is the largest source of atmospheric PAHs (Harvey, 1997). Natural sources include forest fires and volcanic activity. The concentration of atmospheric PAHs is dependent on the types and density of local emission sources, temperature, and meteorological conditions (Harvey, 1997). Due to the increased consumption of fossil fuels for heating, PAH concentration during the winter tends to be higher in colder climates. Atmospheric PAHs rapidly condense onto particles at low temperature. Because of the wide range of vapor pressures, in the temperate atmosphere, three- to four-ring PAHs are in both the gas and the particle phase, whereas five- to seven-ring PAHs are mostly associated with particles (Atlas and Giam, 1989). High percentages of atmospheric PAHs are associated with respirable particulate matter, making the majority of PAHs in the atmosphere potential health hazards (Harvey, 1997). However, atmospheric PAHs undergo various chemical and photochemical degradations. For most PAHs that do not contain cyclopenta fused rings, the important atmospheric gas-phase reactions are with OH radicals and N_2O_5 (Atkinson, 1990). On the other hand, PAHs with cyclopenta fused rings, such as fluoranthene, and some PAHs, such as benzo[a]pyrene, react with O_3 in the atmosphere (Brorstrom *et al*., 1983). Photochemical reactions of PAHs proceed so fast that the atmospheric lifetimes of gas-phase PAHs are generally short (Ohkouchi *et al*., 1999). On the other hand, the PAHs associated with particles such as soot (carbon black) have much longer lifetimes and can be transported long distances (Behymer and Hites, 1985; Kamens *et al*., 1988). The effects of atmospheric particles on human health are related to their penetration depth into the respiratory tract (Wu and Chang, 1997). Small particles, with sizes less than 2.5 μm, readily reach the pulmonary alveolus (Josephson, 1981; Castillo and Jiusto, 1984; Santamaria *et al*., 1990).

Significant concentrations of PAHs are found in soils and sediments throughout all regions of the world. The main source of PAHs in soil is direct spillage of petrogenic products from industrial activities or from vehicles. PAHs in soils in remote regions are

derived primarily from forest fires, atmospheric depositions, and oil seepages. The pattern of PAHs in recent sediments uncontaminated by anthropogenic sources tends to correspond to that of medium-temperature pyrolysis, which indicates an origin primarily from forest fires (Harvey, 1997). Recent studies suggest that most PAHs found in the coastal marine sediments are associated with soot (Gustafsson *et al*., 1997). Biogenic sources have also been suggested as potential sources for some soil/sediment PAHs. Biogenic PAHs originate from biological processes or during the early stages of diagenesis in marine sediments (e.g. perylene; a 4-ring unsubstituted PAH) (Aizenshtat, 1973; Gogou *et al*., 2000).

PAHs are also found in water in detectable concentrations. The sources of PAHs in water include direct fallout of particulate matter from the air, gas exchange with atmosphere, runoff from polluted soils, and direct pollution of rivers and lakes by municipal and industrial discharges. PAHs in water can be taken up by plankton, benthos, and fishes, and may ultimately be consumed by humans. Adamo *et al*. (1997) reported that the exposure of mussels to dissolved PAHs at levels of 5 ng/l caused uptake of PAHs (bioconcentration) which are subsequently transferred to sea bass.

Significant concentrations of PAHs are also detected in common food stuffs. The highest PAH concentrations are mainly found in leafy plants, including tea, tobacco, lettuce, spinach, and in smoked meats and fishes (Baum, 1978; Harvey, 1991). The PAHs in leafy plants are apparently from atmospheric deposition and those in smoked meats and fishes are mostly from *in-situ* production of PAHs during pyrogenesis. Fresh meat and seafood have lower level of PAHs and these PAHs are presumably derived from air and water pollution as well as animal feeds (Harvey, 1997). Tobacco smoke is a complex mixture known to contain more than 150 compounds in the gas phase and more than 2,000 compounds in the particulate phase, including many PAHs. Some of tobacco PAHs are carcinogenic in experimental animals (Hoffmann *et al*., 1978). PAHs are also detected in minerals in association with mercury ores (Blumer, 1975) and in meteorites (Gutman and Cyvin, 1989).

As seen above, PAHs are widespread constituents of the environment (Blumer, 1976; Laflamme and Hites, 1978; Gschwend and Hites, 1981). PAH concentrations in the environment are generally in the range of nanograms per gram or per liter (Kayal and Connell, 1995; Bence *et al*., 1996; Adamo *et al*., 1997; Wilcke, 2000). The latitudinal distribution of PAHs in the deep sea floor is a complex function of emission parameters, the physicochemical properties of PAHs, atmospheric residence times, seawater solubilities, and the microbial degradability of PAHs. PAH distributions are not correlated with annual mean precipitation indicating that the deposition of PAHs is not primarily controlled by wet deposition processes (Golomb *et al*., 1997). It has been suggested that water solubility and octanol-water partitioning coefficients (K_{ow}) play important roles in determining the global distribution of organic contaminants (Wania and Mackay, 1996). The environmental levels of PAHs peaked from 1940 ~ 1950 (Bates *et al*., 1984; Zhang *et al*., 1993) and generally have declined, most likely due to a transition in fuel usage from coal to petroleum and enhanced emission control on automobiles (Latimer and Quinn, 1996; Baumann and Harshbarger, 1998). However, metropolitan and industrialized areas continue to be sources of PAHs (Baker and Eisenreich, 1990; Halshall *et al*., 1994; Coleman *et al*., 1997).

Persistence of PAHs

Due to their hydrophobicity, PAHs are strongly partitioned into sediments and/or lipid-rich biological tissues (Frank *et al*., 1986; Sericano, 1993; Wilson and Jones, 1993; Roper *et al*., 1997; van Hattum *et al*., 1998; Yanik *et al*. 2003). The sorption of PAHs onto particles occurs because of forces such as van der Waal's (Lyman *et al*., 1982) and is substantial for all PAHs limiting the availability of PAHs for other reactions. Sorption coefficients have been highly correlated with the octanol/water coefficient of a compound. Hassett et al. (1980) has suggested the relationship, $\log K_{oc} = \log K_{ow} - 0.317$, for PAHs. PAHs are also semi-volatile and their volatility increases with decreasing molecular weight. Although PAHs, under certain conditions, can be reduced rapidly by photo- or microbial degradation, they may persist for long periods of time in

the environment due to their hydrophobicity and low volatility (Sutherland *et al*., 1995; Yanik *et al*., 2003). If PAHs are strongly bound to soils, PAHs are unavailable for biodegradation even when microbes are capable of degrading PAHs (Erickson *et al*., 1993). The different number of rings and their orientation result in differences in the environmental persistence of PAHs (Ashok and Saxena, 1995). The PAHs formed by fusion of rings in angular fashion, i.e., phenanthrene, chrysene, picene, etc., are more stable than linearly-fused PAHs (Harvey, 1997). The solubility of PAHs tends to decrease with increasing molecular size, although solubility is dependent on molecular symmetry, planarity, and the presence of substituents. Alkylation of PAHs markedly increases the solubility of most PAHs due to the steric interference of planar fused aromatic ring systems and the crystal lattice (Harvey, 1997). Whereas simple PAHs are usually planar, most PAHs are likely to be non-planar (Herndon, 1990). The introduction of alkyl groups into the sterically crowded molecular regions of PAHs, such as the bay region or the fjord positions, causes a distortion from planarity (Harvey, 1997). The carcinogenic and mutagenic properties of PAHs are related to non-planarity (DiGiovanni *et al*., 1983; Harvey, 1991). The low water solubilities, limited volatilities and recalcitrance towards degradation, allow PAHs to accumulate to levels that may exert toxic effects upon organisms (Mix, 1984; Neff, 1985; Onuska, 1989). Bioaccumulation tends to occur more readily with the high molecular weight and less water soluble PAHs (Ashok and Saxena, 1995).

Toxicity

PAHs have long been suspected carcinogens and mutagens (IARC, 1983). There is a general tendency toward acute toxicity for low molecular weight and relatively water soluble PAHs, such as naphthalene (Struble and Harmon, 1983; Darville and Wilhm, 1984), while sub-acute effects such as carcinogenicity and genotoxicity tend to be more representative of high molecular weight and less soluble PAHs (Mortelmans *et al*., 1986; Ashok and Saxena, 1995). The US EPA includes 16 PAHs in the list of priority pollutants to be monitored in aquatic and terrestrial systems (Keith and Telliard, 1979).

Some PAHs such as anthracene, benzo[a]pyrene, and benzo[k]fluoranthene are known to be the primary cancer causing PAHs (Dipple, 1985; Hollender *et al*., 2000). Some volatile PAHs like naphthalene can also be carcinogenic by reacting with NO_3 and forming carcinogenic nitro-derivatives (Arey *et al*., 1989). The association of cancer and chemicals from fossil fuels was first recognized by Sir Percival Pott in 1763 (Pott, 1763), although the specific chemical was not identified. Since Percival Pott discovered chimney sweepers in Britain developed cancer in the scrotum as a result of exposure to soot (Pott, 1763), there have been concerns about the harmful effects of soot and tar (Ramdahl *et al*., 1983). Many studies have been done in order to identify and isolate the constituents of soot, tar and pitch that cause the carcinogenic effects in organisms. Dibenz[a,h]anthracene was the first pure chemical found to possess carcinogenic activity (Kennaway and Hieger, 1930). Cook and coworkers isolated a fluorescent carcinogenic compound from coal tar and identified it as benzo(a)pyrene, a potent carcinogenic PAH (Cook *et al*., 1933). As of 1976, more than 30 parent PAH compounds and several hundred derivatives of PAH had been reported to have carcinogenic effects (NRC, 1972; Dipple, 1976).

PAHs with two to five rings are generally of most concern for environmental and human health effects (ATSDR, 1995). PAHs are absorbed through the skin, lungs, and gastrointestinal tract of organisms (Pickering, 1999). PAHs absorbed into the cell require enzyme modification before becoming biologically active (Haroz, 1983). Some research revealed that the carcinogenicity and mutagenicity of compounds resulted from the oxidized metabolites, not from parent PAHs. Many PAHs function as precarcinogens that require metabolic activation before they are able to bind to DNA, RNA, or proteins (Hall and Grover, 1990). The oxidized metabolites include dihydrodiol, dihydrodiol epoxides, and diol epoxide derivatives of PAHs (Yang *et al*., 1985). Sims and colleagues identified the active metabolites of the PAHs as vicinal dihydrodiol epoxides (Sims *et al*., 1974). The most potent carcinogenicity is achieved when the functional groups are located in the “K-region” or the “bay-region” of the parent PAHs, i.e., in vicinal dihydrodiol epoxides, the epoxide ring is adjacent to the bay region (Jerina and Daly,

1976; Pickering, 1999;Yanik *et al*., 2003). Hecht *et al*. (1985) showed that methyl substitution in the bay-region increases the carcinogenicity of the PAH. The toxicity of compounds is mediated through binding to an intracellular cytosolic protein known as the aryl hydrocarbon receptor (AhR). AhR involves high-affinity binding of the toxicant to the receptor, especially for molecules that are similar to TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) in terms of molecular size, shape, and hydrophobicity (Poland *et al*., 1976; Safe, 1986). A receptor is the reactive structural unit of a cell membrane protein, enzyme, nucleic acid, or other biomacromolecule (Paasivirta, 1991). AhR is a ligand-activated nuclear transcription factor that controls the expression of several genes (Hahn, 1998) and binds to TCDD with high affinity (K_D < 1 nM) (Safe, 1998). Other structurally similar xenobiotics can also attach to Ah receptor. The AhR is activated by binding of halogenated aromatic hydrocarbons including TCDD and planar aromatic hydrocarbons (Hahn *et al*., 1998). Besides planar aromatic hydrocarbons, PCBs can also exhibit a planar arrangement that binds to the Ah receptor. Toxicity depends on the location of the chlorine substituents (Paasivirta, 1991). If a xenobiotic chemical has a similar structure, size, and polarity which fits the receptor, it will affect metabolic pathways after binding to the receptor. Binding of a foreign molecule to the receptor can also disrupt metabolism, thus causing harmful toxic effects on the organisms. Hydrophobic foreign chemicals can be excreted by the organisms only after metabolic transformation to more polar structures. The initial metabolic step is oxygenation by microsomal monooxygenase enzymes. For PAHs, the enzyme is cytochrome P-450 (Polycyclic aromatic hydrocarbons 450) aryl hydrocarbon hydroxylase (AHH) (Paasivirta, 1991). Biotransformation of contaminants means, not only the detoxification and excretion of these compounds but also the formation of reactive metabolites that exhibit their own toxic and carcinogenic characteristics (Malins *et al*., 1984; Varanasi *et al*., 1989). The most well-known carcinogenic PAH is benzo(*a*)pyrene. Chronic exposure to PAHs can also cause dermatitis and hyperkeratosis and possibly affect placental endocrine and hormonal functions (ATSDR, 1995). Many POPs (Persistent Organic Pollutants) have the characteristics of endocrine-like activities. Estrogenic

compounds and chemicals with androgenic/antiandrogenic and thyroid hormone-like activity may cause reproductive and developmental defects in fish and other wildlife populations (Colborn *et al*., 1993). Both estrogenic and antiestrogenic activities associated with PAHs and alkyl phenols have been observed on exposure to the extracts of aquatic and estuarine sediments (Bennett and Metcalfe, 1998; Allen *et al*., 1999; Khim *et al*., 1999).

Because of the persistence, complexity and probable carcinogenicity of PAHs, PAHs have been extensively studied to understand their fate and distribution in the environment and their toxicity in animals and human (Jackson *et al*., 1994; Moore, 1995; Hwang, 2001). Most of the research is aimed at characterizing the distribution of anthropogenic PAHs in environmental matrices, such as sediment/soil, water, organisms, and atmosphere, or their degradation products.

Most source identification is based on mixture composition and geographical distribution. Relatively few studies have been done on the identification of the sources of PAHs using intrinsic stable isotope compositions.

Identifying the Sources of PAHs

PAH concentration and molecular ratios along with other parameters such as, alkane distribution, sterane and terpane biomarker isomeric distributions, have been used to trace, identify, and apportion the sources of complex contaminants mixture in the environment. As mentioned before, combustion products are distinguished from petroleum products by the predominance of high molecular weight 4- to 6-ring PAHs over the lower molecular weight 2- to 3-ring PAHs (Bence *et al*., 1996). They also exhibit a predominance of unalkylated parent compounds over alkylated homologues within each homologues series of PAH, decreasing in relative abundance with increasing levels of alkylation (Badger, 1962; Brassell and Eglinton, 1980; Bjoeseth, 1985; Gonzalez-Vila *et al*., 1991; Theobald *et al*., 1995; Bence *et al*., 1996). The ratio of unstable (kinetic) over more stable (thermodynamic) homologues allows for an evaluation of the contribution of combustion versus petrogenic PAH (Yunker and

Macdonald, 1995). The abundance ratio of the sum of the other three to six ring PAHs to the sum of the alkylated homologues of naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene, can be used to determine if the PAHs are pyrogenic or petrogenic in origin (Wang *et al*., 1999). Some PAHs are relatively resistant to degradation compared with aliphatic hydrocarbons, and the relative amounts can also reflect different sources of hydrocarbon input (Page *et al*., 1996).

Certain PAHs can be used to indicate particular sources. Several PAHs have natural origins and are derived diagenetically from biogenic precursors which are common constituents of higher terrestrial plants (Bouloubassi and Saliot, 1993). Retene (1-methyl-7-isopropyl phenanthrenes) is a characteristic diterpenoid, natural PAH derived from the degradation of abietic acid. Abietic acid is an essential constituent of plant resins, especially conifer resins in temperate region (Simoneit, 1977). Produced by microbially mediated diagenetic reactions of abietic acid, retene is generally considered to be a biomarker for the diagenesis of coniferous materials (Laflamme and Hites, 1978). Formation of retene during conifer forest fires by the thermal degradation of abietic acid has also been reported (Ramdahl, 1983). Some PAHs originate from both natural and pyrolytic sources. Perylene has long been considered an indicator of natural continental inputs and is derived from plant pigments under reducing conditions during plant diagenesis (Aizenshtat, 1973; Gogou *et al*., 2000), but is also a minor component of combustion PAH (Laflamme and Hites, 1978; Venkatesan, 1988). Diatoms appear to contain the major potential precursors for perylene in aquatic systems, although the precise role of diatoms in the adsorption, entrapment and production of perylene is currently unknown (Venkatesan, 1988). PAH in uncontaminated marine sediments contain relatively high amounts of terpene-derived aromatic hydrocarbons, e.g., alkyl-substituted tetrahydrophenanthrenes, indicative of plant fossilization (Laflamme and Hites, 1979; Wakeman *et al*., 1980). Amyrins are pentacyclic triterpenes, and are major components of plant waxes (Brassell *et al*., 1983). The microbially mediated diagenetic alteration of these natural compounds can result in the production of a series of progressively aromatized PAHs (e.g. tetrahydrochrysenes, Bouloubassi and Saliot, 1993).

Phenanthrene and alkylphenanthrenes are generally considered to be of petrogenic origin (Fernandes and Sicre, 1999). Phenanthrene has often been considered a diagenetic in pristine areas (Wakeham *et al*., 1980). Phenanthrene may be a diagenetic product produced by the dehydrogenation of steroids in micro-organisms (Hites *et al*., 1980B; Wakeham *et al*., 1980). Venkatesan and Kaplan (1982) hypothesized the diagenesis of marine lipids in coastal sediments off Alaska was the source of the high relative abundance of phenanthrenes in the area (Fernandes and Sicre, 1999). Anthracene and 2-methylanthracene, 3-ring PAH, are abundant constituent in Tertiary coals (Radke et al., 1990).

Certain PAHs can be used as indicators of each type of combustion when purely anthropogenic combustion takes place (Khalili *et al*., 1995). Fluoranthene and pyrene are characteristic of fuel oil burning (Masclet *et al*., 1986). The association of benzo[ghi]perylene and coronene with vehicle exhaust has long been suggested. The relative proportions of benzo[c]phenanthrenes, benzo[ghi]perylene and coronene in tunnel samples were higher than in other areas (Hangebrauck *et al*., 1967). The absence of alkylated chrysenes and a narrow distribution of n-alkanes (~C15 – C24) are characteristic of diesel and diesel soot (Bence *et al*., 1996).

Concentrations of PAH can be related to their origins by comparing their composition with those of potential sources (Lee *et al*., 1976). The selection of a group of compounds that permits unique identification of contaminant sources and the quantitative apportionment of multiple sources is referred to as chemical fingerprinting (Kennicutt and Comet, 1992). Chemical fingerprinting involves the use of molecular ratios that are both source specific and refractory (Bence *et al*., 1996). In order to evaluate the compositional differences in PAH profiles, the concentrations of PAH are usually standardized into a ratio. Some PAHs like benzo[e]pyrene are frequently used as a reference PAH since it is photochemically stable and predominately found in the particulate phase (Butler and Crossley, 1981). The relative abundances of the alkyl homologues of phenanthrene relative to that of dibenzothiophene have been used to identify different sources in petroleum (Overton *et al*., 1981; Page *et al*., 1995). The ratio

of phenanthrene to anthracene in petroleum is reported to be about 40 – 50 while PAHs from combustion sources have a ratio lower than 10 (Yunker and Macdonald, 1995). The ratio of benzo[e]pyrene to benzo[a]pyrene has been used as an indicator of combustion versus petroleum sources and local versus long range-transport sources (Nielson, 1988). Because benzo[e]pyrene is mostly produced from combustion, a high ratio of benzo[e]pyrene to benzo[a]pyrene may indicate a combustion source. This high ratio also indicates long distance transport because benzo[a]pyrene degrades faster than benzo[e]pyrene. Molecular ratios used for source identification are listed in Table 2.2.

The techniques used for source identification in the environment have been developed over the last 30 years (Bentz, 1976; Overton *et al*., 1981; Volkman *et al*., 1983; Boehm and Farrington, 1984; Page *et al*., 1988; Page *et al*., 1995; Page *et al*., 1996). The major approaches used in source identification include, as shown above, pattern recognition, source-specific diagnostic ratios of PAH analytes, and principal-component analysis (PCA) (Burns *et al*., 1997). The potential problem of using molecular ratios in source identification is alteration of individual compounds relative to each other (Yanik *et al*., 2003). A few studies have shown that with increasing exposure the molecular ratios of isomeric PAHs change systematically in favor of the thermodynamically stable isomers (Gschwend and Hites, 1981; Aceves and Grimalt, 1993). PAH weathering rates are a function of the number of rings and the degree of alkylation (NRC, 1985; Bence and Burns, 1995; Page *et al*., 1995). Weathering causes the lighter, more water-soluble PAHs to decrease faster relative to heavier, less water-soluble PAH (Mahaffey *et al*., 1991). Parent PAHs decrease faster relative to their alkylated homologues (NRC, 1985). For example, alkylated chrysenes are the most stable of the petrogenic PAHs (Bence *et al*., 1996). Chemical and biological change in the concentrations of PAHs can cause considerable difficulties in tracing origins of contaminants in the environment (Yanik *et al*., 2003). In order to overcome these difficulties, more refractory indices should be used to determine the origins of contaminants (Hostettler *et al*., 1999). Source identification using isotopic signature assumes that the compound specific isotope compositions are subject to less chemical

Table 2.2.
Molecular indices for source identification.

Molecular Indices	Note
Methylphenanthrene/phenanthrene	Identify source of hydrocarbon as pyrogenic (less than 2) or petrogenic (Youngblood and Blumer, 1975)
Phenanthrene/anthracene	40 – 50 in petroleum; lower than 10 in combustion sources (Yunker and Macdonald, 1995)
Benzo[e]pyrene/benzo[a]pyrene	Indicator of combustion vs. petroleum sources, high values for combustion sources; local vs. long range-transport sources, high for long distance transport (Nielson, 1988)
Benzo[ghi]perylene/indeno[1,2,3-cd]pyrene	Index of traffic exhaust (Wilcke, 2000)
Naphthalenes/fluoranthene	High for petrogenic sources (Kucklick *et al*., 1997)
Fluoranthene/pyrene	High (more than 1) for pyrogenic sources (Sicre *et al*., 1987)
4-6 ring / 2-3 ring PAHs	High for combustion products (Bence *et al*., 1996)
Pyrogenic index	High for pyrogenic sources; 0.8 – 2.0 for soot samples (Wang *et al*., 1999)
2 – 5 ring PAH, unsubstituted	Combustion sources (Blumer, 1976)
2 – 3 ring PAH, substituted	Petroleum sources (Blumer, 1976)
Alkylated dibenzothiophenes/alkylated phenanthrenes	Identify different petroleum sources (Overton *et al*., 1981)
C2-chrysenes/C1-chrysenes, C2-dibenzothiophenes/C1-dibenzothiophenes	Identify different petroleum sources (Barakat *et al*., 2001)
Fluoranthene and pyrene	Characteristic of fuel oil burning (Masclet *et al*., 1986)
4,5-methylenephenanthrene	Typical pyrolytic products (Lichtfouse *et al*., 1997B)
Benzo[ghi]perylene and coronene	Associated with vehicle exhaust (Hangebrauck *et al*., 1967)
Phenanthrene and alkylphenanthrenes	Petrogenic origins (Fernandes and Sicre, 1999)
Anthracene and 2-methylanthracene	Abundant constituent in Tertiary coals (Radke *et al*., 1990)
Perylene	Indicator of natural continental inputs (Aizenshtat, 1973); diatom contains the precursors for perylene (Venkatesan, 1988); minor component of combustion PAH (Laflamme and Hites, 1978)
Retene	Biomarker for the diagenesis of coniferous materials (Laflamme and Hites, 1978)
Alkylated tetrahydrophenanthrenes	Indicator of plant fossilization (Laflamme and Hites, 1978)
Tetrahydrochrysenes	Indicator of the diagenesis of plant wax (Bouloubassi and Saliot, 1993)
Phenanthrene	Diagenetic product of dehydrogenation of microbial steroids (Wakeham *et al*., 1980)

and biological alteration than traditional molecular ratios and bulk isotopic compositions (Yanik *et al*., 2003).

Compound Specific Isotope Analysis (CSIA)

Carbon has two naturally occurring stable isotopes, ^{13}C and ^{12}C. The ratio of the amounts of these two isotopes may be unique for the compound derived from different sources. When the contaminant enters the environment, it may be possible to identify its source by the stable isotopic composition of individual PAH. Stable isotope ratios are expressed in the per mil (‰) notation:

$$\delta^{N}E = [(R_{sample} / R_{standard}) - 1] \times 1000$$

$$R = {}^{13}C / {}^{12}C$$

Where N is the heavy isotope of element E, and R is the abundance ratio of the heavy to light isotope (Craig, 1957). The international recognized standard for carbon isotopes ($^{13}C/^{12}C$) is PDB, a belemnite from the Cretaceous Peedee formation in South Carolina. Atmospheric nitrogen is the standard for nitrogen ($^{15}N/^{14}N$) because of its homogenous composition. Sulfur ($^{34}S/^{32}S$) isotopes are expressed with respect to the Cañon Diablo troilite. The standard for oxygen and deuterium is SMOW (Standard Mean Ocean Water). Samples are commonly referred to being enriched for that element under investigation if they have more of the heavy isotope than the standard. Samples containing more ^{13}C than the reference compound will have positive $\delta^{13}C$ values and are said to be enriched in ^{13}C. The stable isotopic composition of bulk organic matter is a weighted average of the isotopic compositions of hundreds or even thousands of individual chemical components, each having its own isotopic abundances. To trace the source and history of organic materials, isolation of individual molecular components using various chromatographic techniques is needed. Separation techniques must provide sufficient material for precise and accurate stable isotope analysis. The excellent

resolution provided by fused silica capillary columns makes hydrocarbons and other nonpolar compounds ideal for gas chromatography / isotope ratio mass spectrometry (GC/IRMS) analysis. The combination of a gas chromatograph and an isotope ratio mass spectrometer allows for the rapid, low level measurement of $^{13}C/^{12}C$ ratios in specific compounds. The technique for compound specific isotopic analysis (CSIA) involves coupling a gas chromatograph to a combustion reactor, which is then connected to a stable isotope ratio mass spectrometer. Purified sample mixtures are injected into the column and the compounds in the mixture are vaporized and begin to migrate through a capillary column according to their boiling points assisted by the GC oven temperature program. The compounds in the mixture are then chromatographically separated. The effluent from the gas chromatograph is introduced into a microcombustion / CO_2 purification interface at a temperature of 900°C. The column effluent is combusted to carbon dioxide (CO_2) and water (H_2O) in the interface in the presence of a combination of metal oxide catalyst (copper and nickel). Because of the limited capability of metal oxide to hold oxygen for the combustion of organic matter, metal catalysts need to be frequently re-oxidized, preferably between samples (Merritt *et al*., 1995). For the first couple of minutes, until the solvent is removed from GC column, flow through the combustion reactor is reversed and redirected to a waste vent in order to prevent aging and overloading of the furnace oxidant. Water is removed by cryogenic trap or by a permeable membrane tube externally flushed with helium. High concentrations of carbon dioxide generated during combustion can overload the mass detector electronics of the mass spectrometer (Ellis and Fincannon, 1998). Excess carbon dioxide is removed through an open split prior to entry into the mass spectrometer. Carbon dioxide is introduced into the ion source, where ions are generated under high vacuum by electron impact ionization. The ions are accelerated to an energy up to 10 kV and focused by electronic lenses to form a beam. The ion beam enters the magnetic field and ions are deflected and separated based on their mass number (m/z). The target ion is collected in an ion collector cup and counted. Ion current intensities of masses 44, 45, and 46, which represent the major isotopic forms of CO_2, are measured by mass spectrometer and

recorded simultaneously using a high speed on-line acquisition system. The ratio of the ion current intensities of mass 45 to mass 44 is a measure of the ratio of $^{13}C/^{12}C$ and is interpreted as a $\delta^{13}C$ value by comparison to a reference. Because compounds containing one or more ^{13}C atoms migrate through the gas chromatographic system more rapidly than those containing only ^{12}C, $^{13}CO_2$ (mass 45) precedes $^{12}CO_2$ (mass 44) at the ion source by 10 to 100 milliseconds. In complex mixtures, where two or more peaks elute close together, the isotopically light tail of the first component underlies the beginning of the second peak, and the isotopically heavy front of the second peak underlies the end of the first peak (Hayes *et al*., 1990). Because of this effect, high purity of samples is very important during CSIA and baseline resolution of compounds is preferable. A minor component co-eluting with a target compound can have a significant effect on the isotope ratio if their carbon isotopes are significantly different (Merritt *et al*., 1994; Ricci *et al*., 1994; Ellis and Fincannon, 1998). Thus to improve the accuracy of isotope measurements, interference are removed such as co-eluting compounds or unresolved complex mixtures (Ellis and Fincannon, 1998). The purer the analyte introduced into the GC, the less the problems of co-elution, peak overlap, and UCM bleed. The use of internal standards with known isotopic compositions provides further verification of instrumental performance. This GC/IRMS combustion technique allows for the sensitive detection of $^{13}C/^{12}C$ ratios at subnanomolar concentrations.

Because of the use of different reactants and different production processes, PAHs produced from different sources should have unique stable isotopic compositions that can be used to identify sources (O'Malley *et al*., 1994; Ballentine *et al*., 1996; O'Malley *et al*., 1996; O'Malley *et al*., 1997; McRae *et al*., 1999; Yanik *et al*., 2003). The importance of using the stable carbon isotope ratio of individual PAHs for source identification has been addressed by a few researchers. Compound specific isotope analysis of PAHs was first used to identify anthropogenic sources of PAHs in complex mixtures such as various soots and oils in urban environments and estuaries (O'Malley *et al*., 1994). They concluded that no significant isotopic fractionation, vaporization, or photolytic decomposition reactions occurred in 2-, 3-, 4-, and 5-ring PAHs during

environmental transport. O'Malley *et al*. (1997) reported that different isotopic signatures were produced during the burning of different kinds of biomass, C3 and C4 plants, which involved different isotope fractionations during the initial carboxylation step in the photosynthetic pathway. McRae *et al*. (1999) also used compound specific isotope analysis to differentiate coal-derived PAHs from different processes and used it to apportion sources.

The stable isotopic composition of a pollutant in the environment is the end-result of a complex chain of events. Once the contaminant is released to the environment, it is then subject to a redistribution throughout various matrices including air, water, sediments and biological tissues depending on its chemical properties and stability. The partitioning of the chemical among these various phases may be accompanied by isotope fractionations as well as chemical transformations. Environmental transformations are brought about by physical, chemical and microbiological processes. Each process may define an independent set of isotopic and compositional changes. It has not been clearly established whether chemical and biological alterations affect the isotopic signature of individual PAHs. However, isotopic fractionation by biodegradation may be predictable because microorganisms tend to preferentially utilize the isotopically depleted molecules (Yanik *et al*., 2003). It is known that many PAHs are biodegraded with the smaller PAHs preferentially degraded (Mahaffey *et al*., 1991). A combination of compositional and stable isotope changes may be linked to specific events and processes. By analyzing contaminant samples at different stages of transport, it should be possible to understand those processes that act on them and to elucidate the complex chain of events which led to the observed stable isotopic compositions of contaminants. Yanik *et al*. (2003) monitored the isotopic composition of PAHs in a controlled experiment, where the PAHs, mostly alkylated naphthalenes, dibenzothiophenes, anthracenes, and phenanthrenes, were exposed to a variety of conditions over time. The research showed that biodegradation has an effect on the isotopic composition of individual PAH molecules with a trend toward isotopic enrichment in the residual PAH. Isotopic compositions changed by 2 to 8‰, indicating enrichment is caused by biodegradation.

Stable isotope analysis may be useful as an effective tracer to apportion the sources of contaminants in the environment. With the increasing need to understand the dynamics of contaminated sites, a more powerful and accurate analytical tools is needed. Compound specific isotopic analysis is a possible new tool that can be used to answer these difficult and complex questions (O'Malley *et al*., 1994; Dowling *et al*., 1995; O'Malley *et al*., 1996; Kelley and Hammer, 1997; Jarman *et al*., 1998).

CHAPTER III

METHODS

PAH Quantification

General analysis procedures for the determination of PAHs in environmental samples include three major steps; sample extraction, sample clean-up and instrumental analysis. Fig. 3.1 illustrates the overall analytical procedures for PAHs quantification. All glasswares used for the analysis, except purification columns, were cleaned by washing with Micro cleaning solution, rinsing with tap water, and baking at 400˚C for 4 hours. Purification columns were washed with Micro cleaning solution and tap water and then rinsed with solvents in the order of methanol, dichloromethane and hexane. All solvent used were of high purity (more than 99.9%) and the purity was checked after 500-fold concentration.

Extraction and Clean-up

An aliquot (approximately 15 g) of partially dried sediment sample was mixed with a sodium sulfate drying agent and, then extracted on an accelerated solvent extractor (ASE) with dichloromethane. The ASE method allows for a heating period of 5 minutes followed by a static extraction of 5 minutes at 1500 psi and 100ºC. After this cycle, fresh solvent was added to the extraction cell and a second static extraction was initiated to complete the extraction. Total time for a single sample extraction was about 20 minutes. Prior to extraction, samples including QA/QC samples, were spiked with surrogate internal standards. The surrogate internal standard mixture contains 5 deuterated PAHs (d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene and d12-perylene). The ASE extracts were concentrated in a water bath at 55 ˚C and the solvent was exchanged into 2ml of hexane. The concentrated extracts were then introduced onto an alumina/silica gel chromatographic column to remove interfering compounds (e.g., polar lipids). Alumina oxide (Aldrich, ~150 mesh) was activated by heating at 400˚C for 4

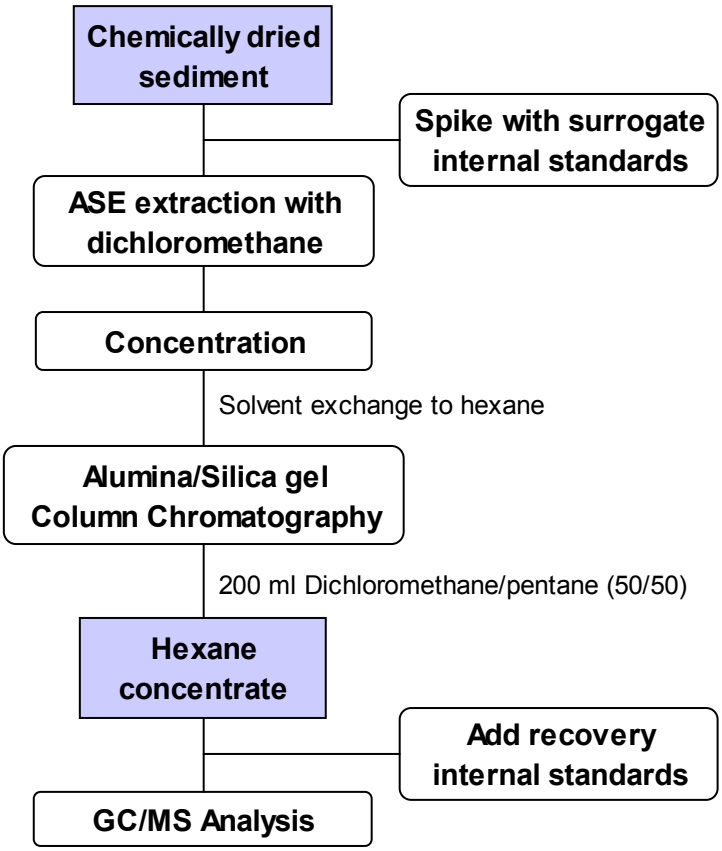


Fig. 3.1. Analytical procedure for PAH quantification.

hours and then deactivated with HPLC grade water (1% w/w). Silica gel (Aldrich, 100 ~ 200 mesh) was activated by heating at 170˚C for 12 hours and deactivated with HPLC grade water (5% w/w). The column was packed with glass wool, 5 g of sand, 10g of deactivated alumina, 20 g of deactivated silica gel slurry in pentane, and 3 g of anhydrous sodium sulfate. 50 ml of pentane was added and drained to the top of the sodium sulfate to condition the column. The extracts were then transferred to the column and eluted from the column with 200 ml of 1:1 (v/v) pentane – dichloromethane mixture solution. The collected solvent was concentrated and exchanged to 1 ml of hexane for instrumental analysis. In order to determine surrogate recovery, additional internal standards were added to the final purified extracts. The recovery internal standard contains d10-fluorene and d12-benzo[a]pyrene.

Instrumental Analysis

Analysis of PAHs was performed with an Hewlett Packard 6890 gas chromatograph coupled with an Hewlett Packard 5973 mass selective detector. Separation of PAHs was accomplished with a 30 m × 0.25 mm i.d., 0.25 μm film thickness, fused silica capillary column with DB-5MS (methylpolysiloxane, 5% phenyl) bonded phase (J&W Scientific). The injection port was operated in a splitless mode for 2 min at 270˚C. The oven temperature was programmed to increase from the initial temperature of 60 ˚C to 150 ˚C at 15 ˚C/min, then 5 ˚C/min to 220 ˚C, and then 10 ˚C/min to a final temperature of 300˚C with a final holding time of 10 min. The chromatographic column effluent was introduced into the 70-eV electron impact mass spectrometer through 300˚C transfer line. The detector was operated in selected ion mode (SIM) to maximize sensitivity. GC/MS operating conditions are summarized in Table 3.1. The GC/MS was calibrated using standard compounds at five different concentration levels ranging from 5 to 200 ng/ml of each analytes prior to sample analysis. The response factor for each PAH compound was calculated from the five calibration standard runs for each compound based on the five deuterated surrogate internal standards. Concentrations of PAHs in sample extract were then calculated using the average response factor for each analyte. All data were

Table 3.1.
GC/MS operating conditions for PAHs quantification.

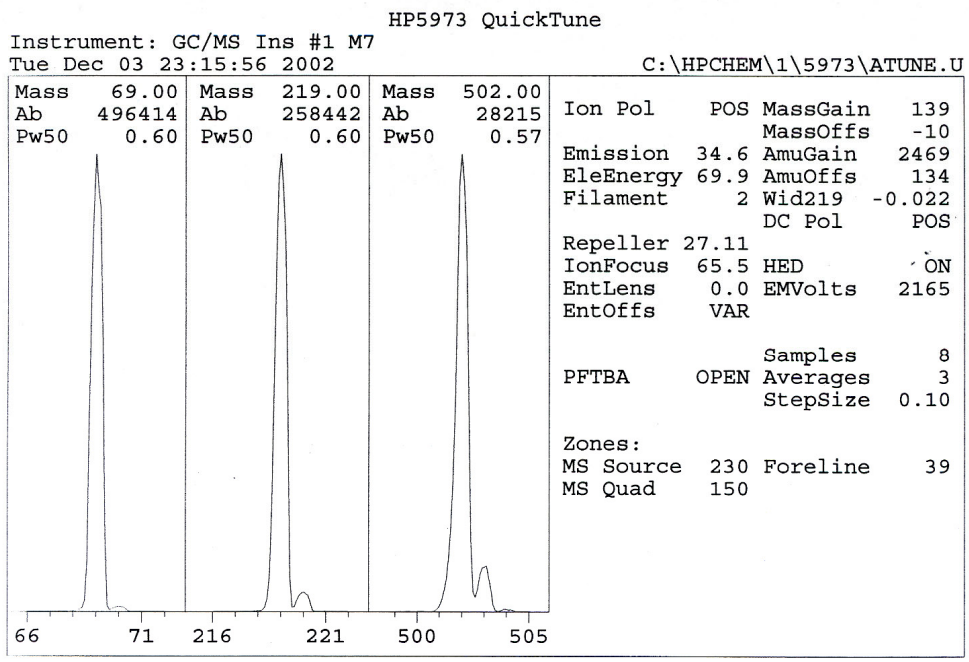
GC	HP 6890 series
Detector	HP 5973 mass selective detector
Software	HP ChemStation G1701BA Version B.01.00
Carrier gas	Helium, 0.4 mL/min
Injector temperature	270 ˚C
Injection volume	2 µl
Injection mode	Splitless (2 min)
Column	Fused silica capillary DB-5MS (J&W Scientific) 30 m × 0.25 mm ID, 0.25 µm film thickness
Temperature program	60 ˚C to 150 ˚C at 15 ˚C/min 150 ˚C to 220 ˚C at 5 ˚C/min 220 ˚C to 300 ˚C at 10 ˚C/min, 10 min hold
Total run time	38 min
Transfer line temperature	300 ˚C
Acquisition mode	Selected ion monitoring (SIM)
Ionization source	Electron impact (70 eV)
MS source temperature	230 ˚C
MS quardropole temperature	150 ˚C
Solvent delay time	5 min
Mass scan time	50 scan/sec

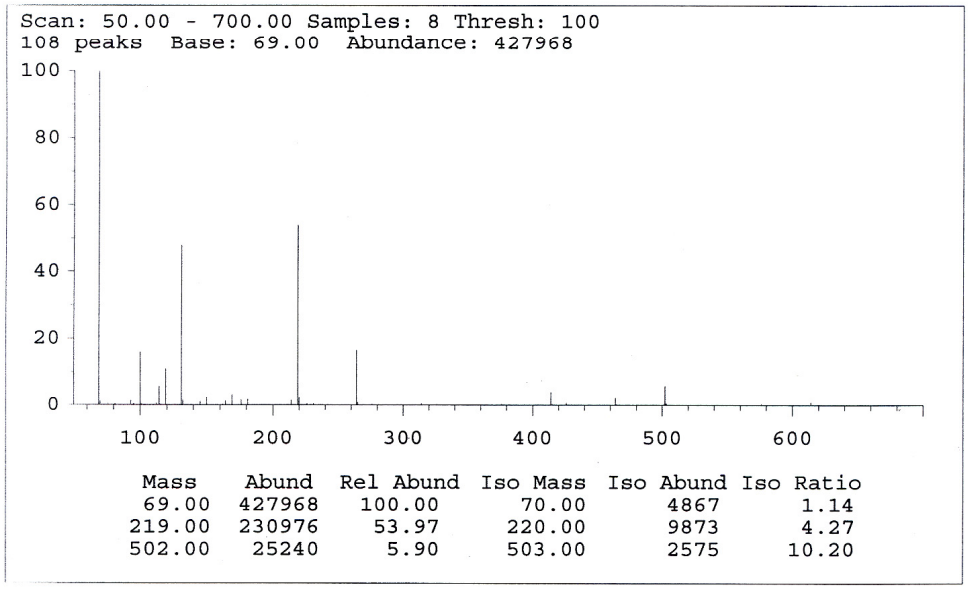
corrected for the recovery of surrogate compounds. A calibration check standard was run three times in each sample sequence to confirm that the instrument responses remained within the calibrated range and to verify chromatographic performance (continuing calibration). Response factors for each analyte in the continuing calibration standard must fall within the acceptance criteria, which is a relative standard deviation (RSD) of less than 20 % of the initial calibration. Before starting an analytical measurement, the MS detector was tuned using PFTBA (perfluorotributylamine) to ensure proper mass spectrometric response. Fig. 3.2 shows a standard tune result. Each of the peaks representing PAHs was identified by mass spectrum of selected ions and the retention time of the quantitation ion (molecular ion) relative to the initial calibration standard. Typical ion chromatograms and mass spectra, along with total ion chromatogram (TIC) are shown in Fig. 3.3. Both parent and alkylated homologues were measured. Target PAHs, quantification / confirmation ions, and method detection limits are listed in Appendix A.1.

Compound Specific Isotope Analysis (CSIA)

Extraction and Purification

Chemically dried sediments (about 15 g) were extracted on ASE system with dichloromethane. Operational conditions for ASE are the same as in the PAH quantification method above. For some sediments which had low concentrations of PAH requiring the extraction of large amounts of sediment, 50 ~ 100 g of chemically dried samples were Soxhlet extracted for 24 hours with 500 ml of dichloromethane. The extracts were concentrated into 2 ml of hexane in a water bath at 55 ˚C. Concentrated extracts were first separated based on compound class into aliphatic and aromatic fractions using alumina / silica gel column chromatography as in the PAH quantification method, except for the elution sequence. Aliphatic hydrocarbons were eluted from the column with 100 ml of pentane. Aromatic hydrocarbons were then eluted with 200 ml of 1:1 (v/v) pentane – dichloromethane. The pentane – dichloromethane extract primarily contains the aromatic hydrocarbons, including PAHs, PCBs, and impurities. The





Mass	Abund	Rel Abund	Iso Mass	Iso Abund	Iso Ratio
69.00	427968	100.00	70.00	4867	1.14
219.00	230976	53.97	220.00	9873	4.27
502.00	25240	5.90	503.00	2575	10.20

TARGET MASS:	50	69	131	219	414	502
DYNAMIC ENT OFFSET:	9.8	10.8	10.8	12.5	12.3	17.1
TARGET ABUND(%):	1.0	100.0	45.0	50.0	3.5	5.0
ACTUAL TUNE ABUND(%):	0.9	100.0	47.9	54.0	4.2	5.9

Fig. 3.2. MSD standard tune result. PFTBA (perfluorotributylamine) was used as an instrument tuning standard.

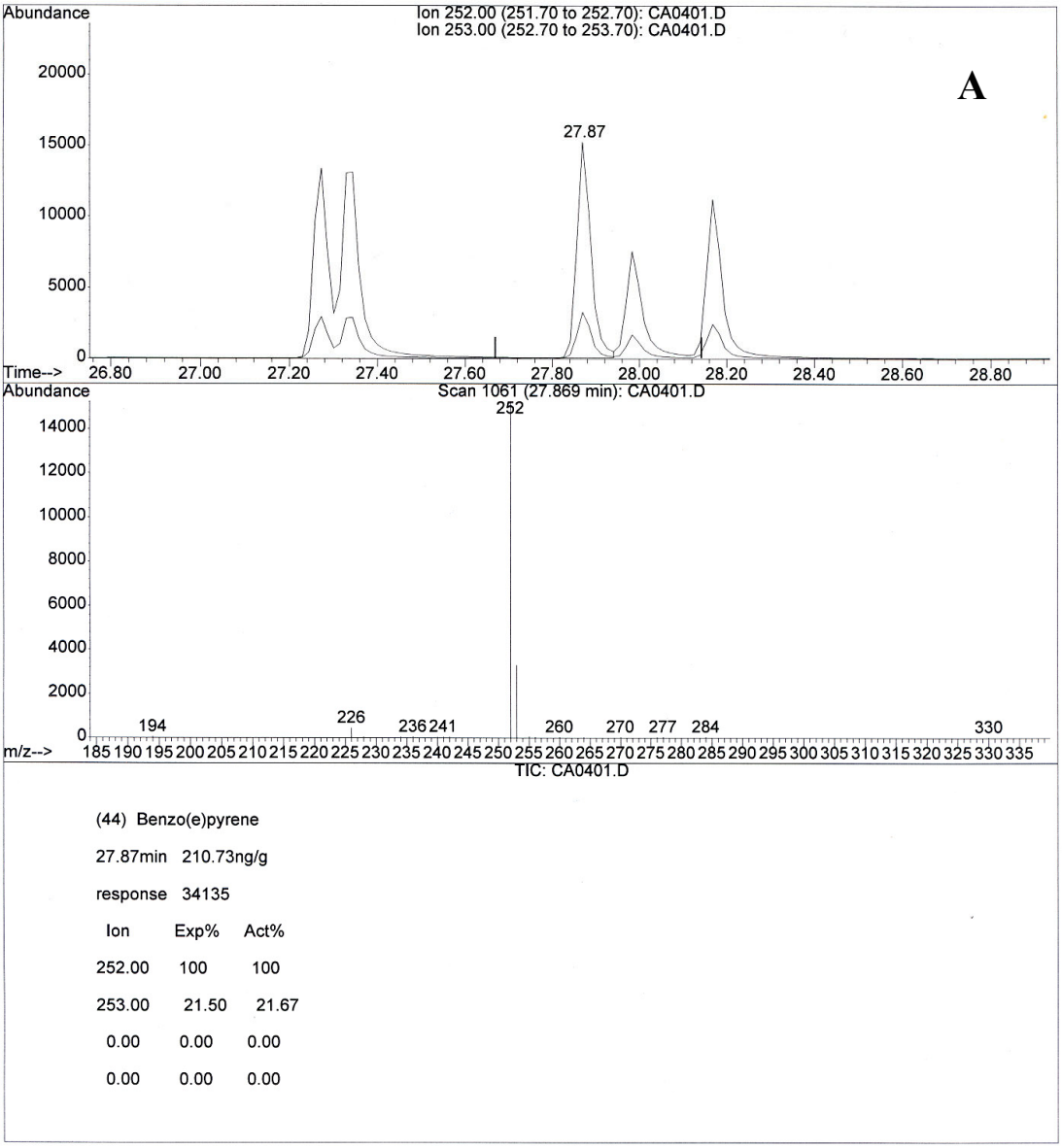


Fig. 3.3. Example of ion chromatogram and mass spectra of selected ions for benzo(e)-pyrene (A) and total ion chromatogram (B).

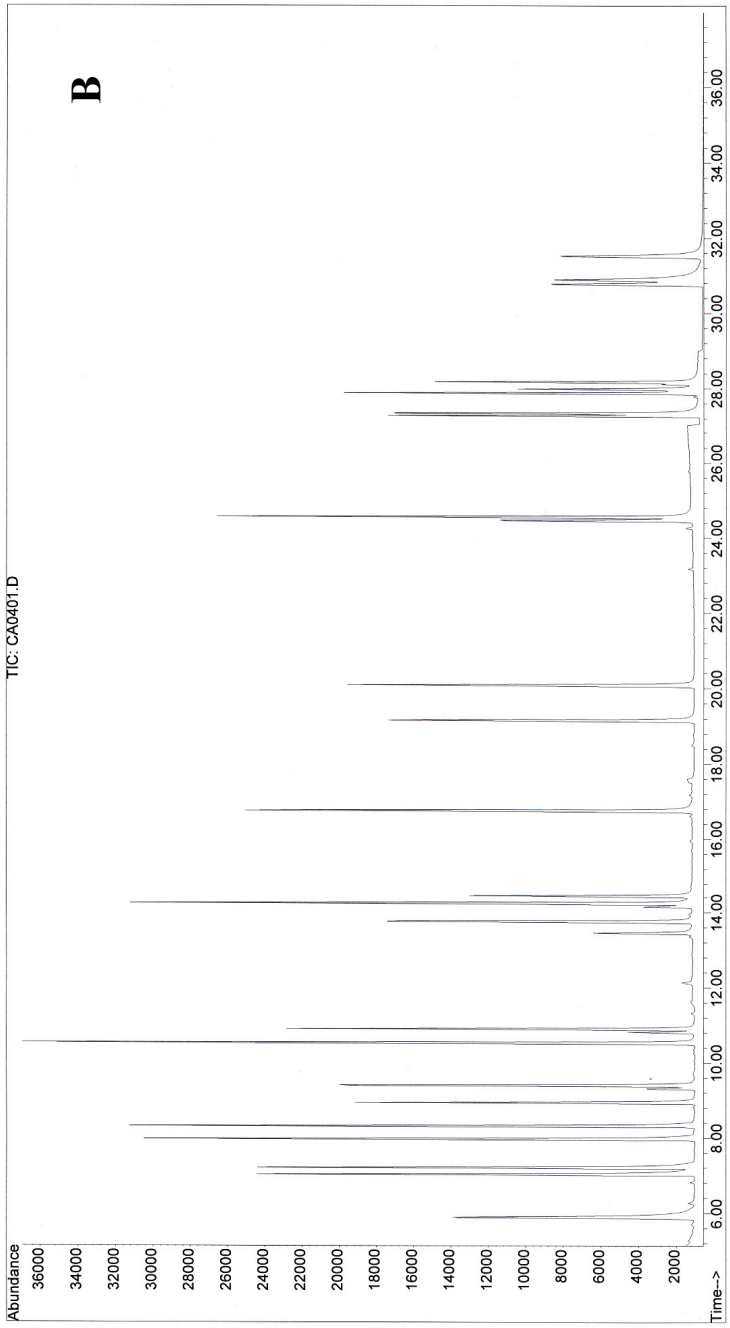


Fig. 3.3. Continued.

fractions were then concentrated to 1 ml using Kuderna – Danish tubes heated in a water bath at 55 ˚C. The aromatic hydrocarbon fraction was then further purified by an automated gel permeation chromatography (GPC) (Krahn et al., 1988) using high performance liquid chromatography (HPLC) with a precolumn (8 × 50 mm Phenogel 100 Å) and two size exclusion columns (22.5 × 250 mm Phenogel 100 Å), which can isolate PAH fractions by size difference (size exclusion chromatography). A SpectraSeries P1000 HPLC system (Thermo Separation Products) with an autosampler (SpectraSeries AS100, Thermo Separation Products) interfaced to a UV-VIS detector (SPD-10A vp, Shimadzu) was used. Dichloromethane was used as mobile phase. PAH fractions were collected in 60 ml vials using an automated fraction collector (2211 Superrac, LKB Bromma). Collected fractions were concentrated to 1 ml of dichloromethane.

This procedure above was initially used to separate PAHs from other interfering compounds for stable isotope ratio analysis. However, further development of purification procedures was required to obtain more pure isolates. In order to achieve better purity for isotopic analyses, more purification procedures, like thin layer chromatography and carbon/silica column chromatography were tested. Following GPC, the PAH fraction was further purified by thin layer chromatography (TLC). The silica gel TLC plate (60 Å, 500 μm thickness, EM Science) was prewashed by developing with 1:1 (v/v) dichloromethane – methanol mixture and then activated by heating at 120 ˚C for 1 hour. After cooling in the desiccator, about 100 μl of extract was applied as a thin band onto the TLC plate using a micropipette. The initial sample band was focused as a very narrow streak by developing with dichloromethane to the upper edge of initial sample band. After drying of application solvent, the plate was developed with 3:2 (v/v) cyclohexane – toluene mixture and the required PAH band (R_F ~ 0.81) was located using short wavelength (254 nm) UV light by comparison with the development of standard materials. The silica gel containing the PAHs was scraped off and the PAHs were extracted with dichloromethane by sonication for 30 min three times. The extract was then filtered and rinsed through a small column constructed by filling with glass wool,

sand and sodium sulfate in order to remove silica gel and moisture. The filtrates were then concentrated to 100 μl ~ 1 ml of hexane depending on the PAH concentration for isotope ratio analysis.

Following GPC, carbon/silica gel column chromatography was also tested for the removal of other impurities based on the PAHs' planar structure. The concentrated extracts after GPC were introduced to 1:20 carbon/silica gel chromatographic column in order to remove other nonplanar interfering compounds. Carbon powder (J.T. Baker) was rinsed with methanol three times and then activated by heating at 130˚C for a minimum of 72 hours. Silica gel (Aldrich, 70~230 mesh) was activated by heating at 170˚C for 16 hours. The column was packed with glass wool, 2 cm of anhydrous sodium sulfate, 2 g of 1:20 (w/w) carbon – silica gel mixture and 2 cm of anhydrous sodium sulfate. 40 ml of 1:4 (v/v) dichloromethane – cyclohexane mixture was added and drained to the top of the sodium sulfate to rinse column. The extracts were then transferred to a column and the first fraction was eluted from the column with 30 ml of 9:1 (v/v) dichloromethane – toluene mixture solution. The second fraction was then eluted with 30 ml of toluene. The collected solvent was evaporated and concentrated by rotary evaporator to approximately 1 ml for instrumental analysis.

Because of the low recovery of some high molecular weight PAHs in carbon/silica gel column chromatography, some modification of the carbon/silica gel column was made. The concentrated extracts after GPC were introduced to 5 % (w/w) carbon/silica gel chromatographic column in order to remove other nonplanar interfering compounds. Carbon powder and silica gel was rinsed and activated in the same way as in the carbon/silica gel column chromatography above. The column was packed from bottom to top with glass wool, 0.5 cm of anhydrous sodium sulfate, 2 g of 5 % (w/w) carbon – silica gel mixture, 2 cm of activated silica gel, and glass wool plug. The column was rinsed with solvents in the order of 15 ml toluene, 40 ml dichloromethane, 30 ml of cyclohexane and 30 ml of pentane. The extracts were then transferred to a column and the first fraction was eluted from the column with 40 ml of pentane in order to remove non-planar impurities. The second fraction was eluted with 40 ml of toluene and then the

column was flipped and eluted again with 60 ml of toluene. The collected solvent was evaporated and concentrated by rotary evaporator to approximately 1 ml for instrumental analysis.

Gas Chromatograph / Combustion / Isotope Ratio Mass Spectrometry (GC/C/IRMS)

After final separation and purification, the analytes of interest were taken up in an appropriate solvent to a concentration in the 5 ~ 100 ng/μl range, depending on the sensitivity of the instrument for particular compounds. Samples were analyzed using a Varian 3400 gas chromatograph coupled to a Finnigan MAT 252 mass spectrometer. A DB-5MS fused silica capillary column (30m × 0.32 mm i.d., 0.5 μm film thickness, J&W Scientific) was used to chromatographically separate the PAHs. The injection port was operated in the splitless mode for 50 seconds at 270˚C. The initial oven temperature of 60˚C was held for 1 min. The oven was programmed to increase from 60 ˚C to 150 ˚C at 12 ˚C/min, then 5 ˚C/min to a final temperature of 300˚C with a final hold time of 20 min. GC effluents were passed through a combustion interface at 980˚C, quantitatively combusting the PAHs to carbon dioxide. The effluent was continuously introduced into the inlet system of a Finnigan MAT 252 isotope ratio mass spectrometer. Sample components were then analyzed for stable isotopic composition. The combustion furnace was reoxidized for 5 min before the injection of each sample. Before starting an analysis, the IRMS was tuned by focusing the ion source for maximum ion current output and by peak centering for mass 44 in order to ensure stable and accurate isotopic abundances. The $\delta^{13}C$ isotopic ratios of individual PAHs in the sample were determined by comparison to a working standard of CO_2 (99.996 %, $\delta^{13}C_{PDB} = 11.57$ ‰) introduced in triplicate at the beginning of each run by means of an open split and subjected to the same condition as the samples.

Quality Control

For quality assurance and quality control, each set of samples was accompanied by a procedural blank, a matrix spike and a duplicate sample, which were carried throughout

the entire analytical procedure in a manner identical to the samples. A procedural blank was used to check for background contamination during the extraction and purification steps. The concentration in the procedural blank must be less than the method detection limit. A matrix spike was used to evaluate for bias and duplicates were used to evaluate the precision of the analysis. Certified standard reference materials were analyzed as additional quality assurance checks. A laboratory reference sample (diluted oil sample) was analyzed with each batch of samples to confirm GC/MS/SIM system performance and calibration. Recoveries of surrogates and spikes were verified. Instrumental calibrations were checked by reinjection of the original calibration mixtures (continuing calibration). The GC/MS calibration was verified before, during and after each analytical sequence, and the calibration check was maintained within ± 15 % for all analytes of interest. All QC values must meet established acceptance criteria (Table 3.2). If the criteria were not met, corrective action was taken and samples were re-extracted.

For isotope ratio measurement, the IRMS was routinely tested for resolution, system and signal stabilities, relative and absolute sensitivity, peak flatness and ratio linearity as per the operational manual (Finnigan MAT 252). All sample isotope values were calculated based on a standard gas injected at the beginning of each sample run. Standard reference material of known isotope ratio was included in each analytical sequence to check the bias of isotope ratio measurement.

Table 3.2.
QA/QC acceptance criteria for PAH analysis.

Surrogate Recovery	Low High	75 % 120 %
Blank	Upper Limit	MDL
Duplicate	RPD Limit	25 %
Matrix Spike / MS Duplicate	Spike Recovery Low Spike Recovery High RPD Limit	75 % 120 % 25 %
Standard Reference Material	Acceptance Range	- 35 % to + 35 %
GERG Standard oil Check	Acceptance Range	- 35 % to + 35 %
Calibration Check	Lower Upper	- 15 % + 15 %

CHAPTER IV

DEVELOPMENT OF PURIFICATION AND COMPOUND SPECIFIC STABLE CARBON ISOTOPE ANALYSIS METHODS

Environmental samples, including sediments and soils, can contain varying amounts of many types of organic matter. To trace the source and history of organic materials in the environment, compound specific stable carbon isotope ratios can be effective. In order to accurately determine the stable carbon isotope ratio of specific compounds, it is necessary to extract, isolate and purify the constituent components using various chromatographic techniques to avoid co-elution, peak overlap and UCM interferences during isotopic analysis. Coeluting compounds can have effect on the observed isotope ratio of targeted compounds, if the coeluting compounds have significantly different isotope values (Merritt *et al*., 1994; Ricci *et al*., 1994; Ellis and Fincannon, 1998). Obtaining high purity samples, that have not been modified in isotopic composition, is important for accurate analysis. Separation techniques must also provide sufficient material for precise and accurate stable isotope analysis.

Purification and isotope analysis methods were developed in order to more accurately measure the stable carbon isotope ratio of PAHs in environmental samples. Sample extracts were purified and separated into several fractions by column and high performance liquid chromatographic (HPLC) techniques. Method refinement was directed towards improving compound separations using purification techniques and high resolution chromatographic columns. While GC/MS quantification of PAHs requires only moderate purification because selected ions are measured for the quantification, it is important for measuring accurate isotope ratio in GC/IRMS analysis (Meier-Augenstein, 1997; Ellis and Fincannon, 1998). Development of the methods can be accomplished by improving accuracy and precision of isotopic measurement by removing interference from co-eluting compounds or unresolved complex mixtures. Method accuracy and precision were verified using authentic standards. Purity of

isolates was also verified by gas chromatography with flame ionization detection and mass spectrometry. The analytical protocols were evaluated to ensure that compositional and stable isotopic integrity has been preserved by processing authentic analyte standards of known stable isotopic composition throughout the entire analytical protocol.

The procedures used to separate and purify various classes of contaminants for stable carbon isotope ratio analysis are shown in Fig. 4.1. The purification procedure involves alumina/silica gel column chromatography, gel permeation chromatography, carbon/silica gel column chromatography, and thin layer chromatography. Sample extracts were first purified by alumina/silica gel column chromatography. The alumina/silica gel column separates compounds based on polarity and separates aromatic from aliphatic hydrocarbons using variable eluting solvent systems. Due to high concentration of aliphatic hydrocarbons in environmental samples and their coelution with PAHs during GC chromatographic separations, it is necessary to remove aliphatic hydrocarbons prior to isotope ratio analysis. In order to determine the necessary volume of pentane for the elution of aliphatic hydrocarbons, multiple alumina/silica gel columns were tested using PAH standards of different concentration (120 ng ~ 6000 ng) of individual PAH compound. The cumulative recoveries of PAH compounds in pentane elution and recoveries of the compounds in the 100 ml pentane fraction are shown in Fig. 4.2 and 4.3, respectively. Except for naphthalene, all compounds tested had losses of less than 3 %. Although naphthalene showed loss of 5 %, no isotopic fractionation was detected. It is usually recommended that 50 to 80 ml pentane be used to remove aliphatics. However, since there was no loss of aromatic compounds, it is preferable to use more pentane to ensure the removal of all interferences. Thus for this study, 100 ml of pentane was used to elute all aliphatic hydrocarbons from the sample extracts. After pentane elution, the column was then eluted with 200 ml 50/50 (v/v) dichloromethane/pentane. The recovery of model PAH compounds after alumina/silica gel column chromatography are shown in Fig. 4.3. Except for dibenzothiophene, which has recovery of 82%, all PAH compounds had recoveries greater than 90%.

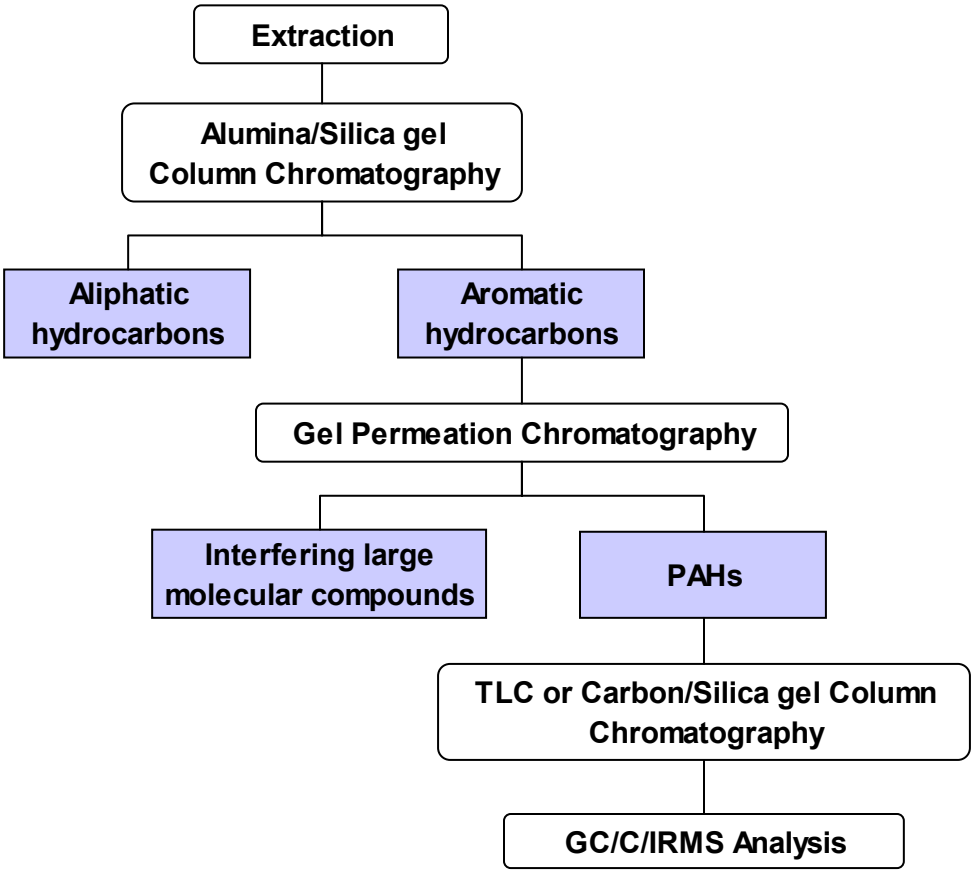


Fig. 4.1. Analytical procedure for stable carbon isotope ratios of PAHs.

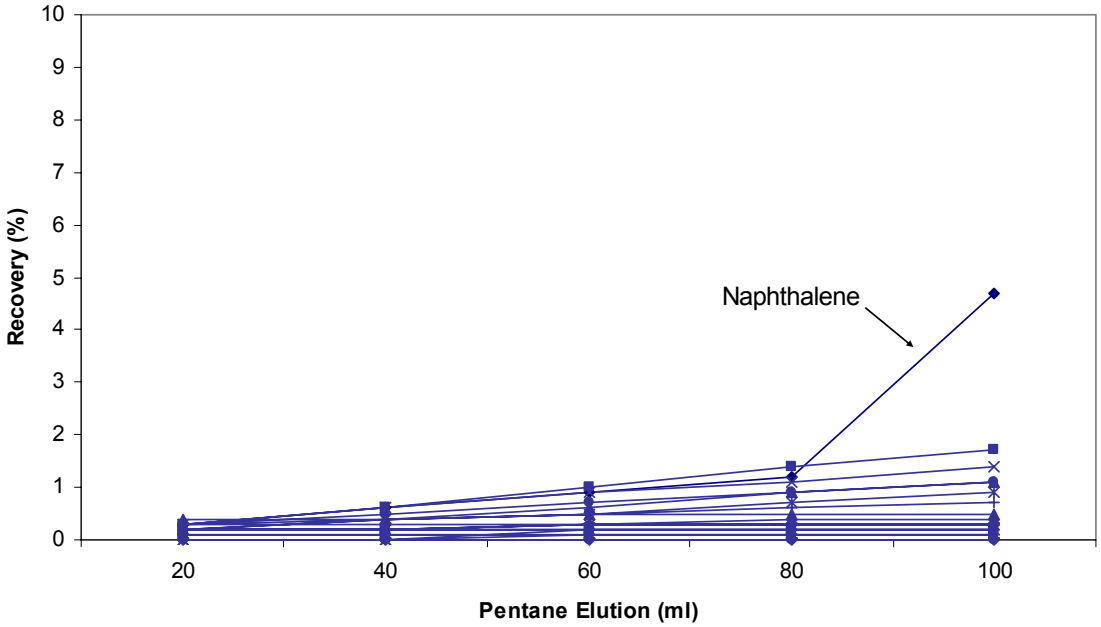


Fig. 4.2. Cumulative recoveries of PAHs in pentane fractions.

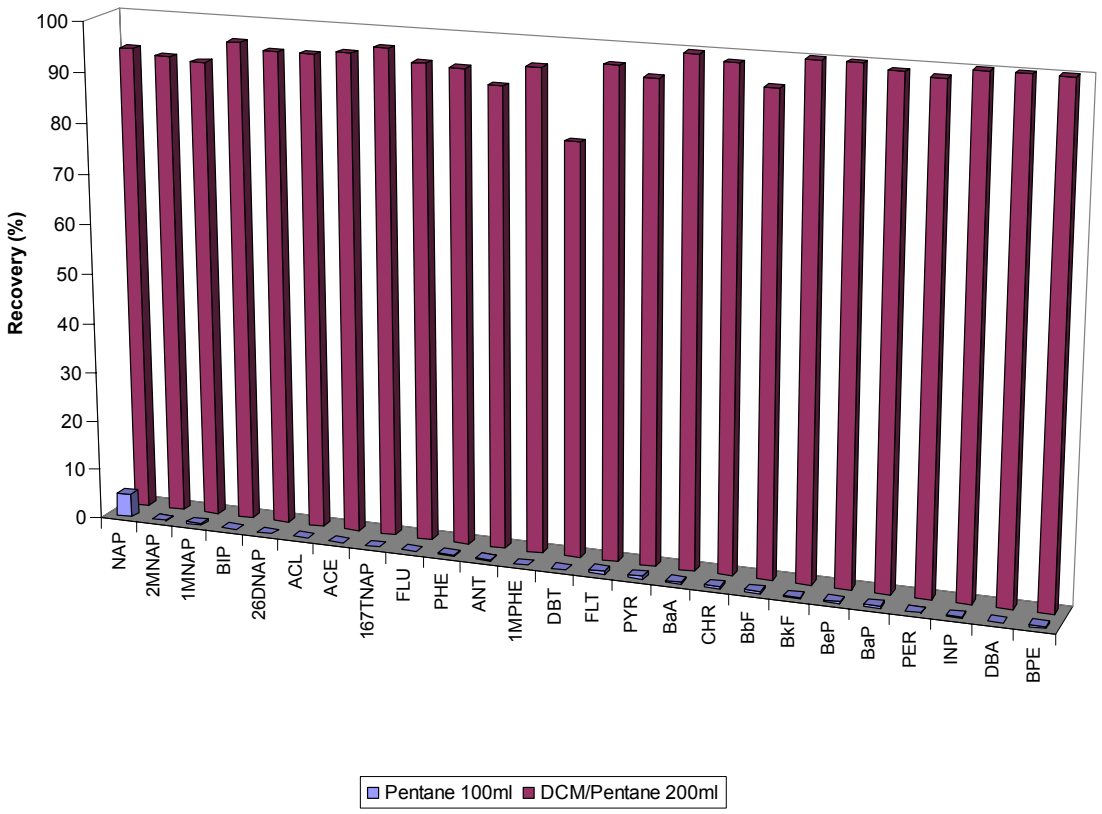


Fig. 4.3. Recoveries of PAH compounds after alumina/silica gel column chromatography.

After Al/Si gel column chromatography, sample extracts were further purified by gel permeation chromatography. For gel permeation chromatography a HPLC system with Phenogel 100 Å molecular sieve columns was used to separate compounds based on molecular size or molecular volume (size exclusion chromatography). Because of the small and compact structural characteristics of PAH compounds, they can enter into small pores in molecular sieves and thus are retained in the column more than compounds of higher molecular size. Mostly linear structure impurities elute in the first stage of chromatographic elution and PAH compounds are collected 13.9 to 21.0 minutes after the injection of sample. Collection start and end time is monitored by detecting PAHs using a UV-VIS detector. All PAH compounds experienced little losses during gel permeation chromatography with recoveries of more than 90 % for most compounds (Fig. 4.4). In the early eluting fraction (0 to 13.9 min) no PAHs were detected (less than 0.1 % recoveries).

PAHs exhibit planar structural characteristics. Because of the planar structure of PAHs, it is possible to use a carbon column to separate PAHs from non-planar molecules. The carbon column chromatography included elution with 40 ml pentane (fraction 1), then 30 ml of dichloromethane/toluene (9/1) to remove non-planar compounds (fraction 2), and a final 30 ml toluene elution to recover planar PAH compounds (fraction 3). This method was originally developed to separate planar and non-planar polychlorinated biphenyls (PCBs). In the first pentane elution, recoveries of PAHs were less than 0.1 % for individual PAH compounds. However, PAHs expected to be detected only in the third fraction were recovered in the second as well as the third fraction. In addition, high molecular weight PAHs like chrysene, benzofluoranthenes, and benzopyrenes, did not elute from the column, possibly due to their high affinity for carbon, even using 100 ml of toluene for elution (Fig. 4.5). Because of the low recovery of high molecular weight PAHs on carbon/silica gel column, new carbon chromatographic column technique was tested. The method tested was originally developed to purify samples for the analysis of polychlorinated dibenzodioxins or dibenzofurans. In this method, sample extracts were first eluted with pentane to remove non-planar impurities, 40 ml of toluene, and then the

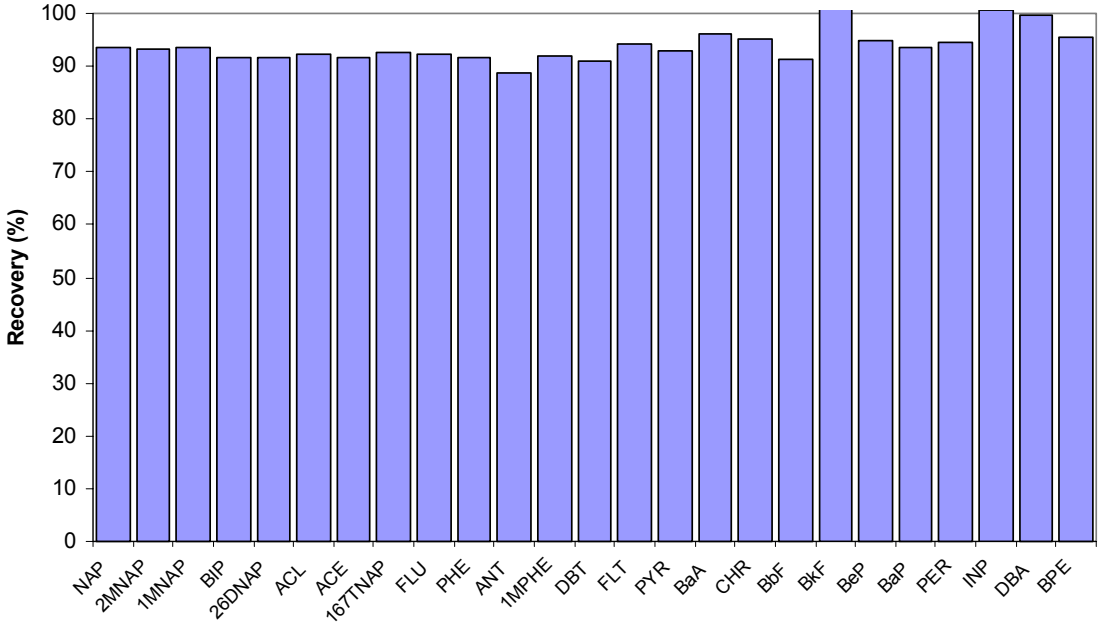


Fig. 4.4. Recoveries of PAH compounds after gel permeation chromatography.

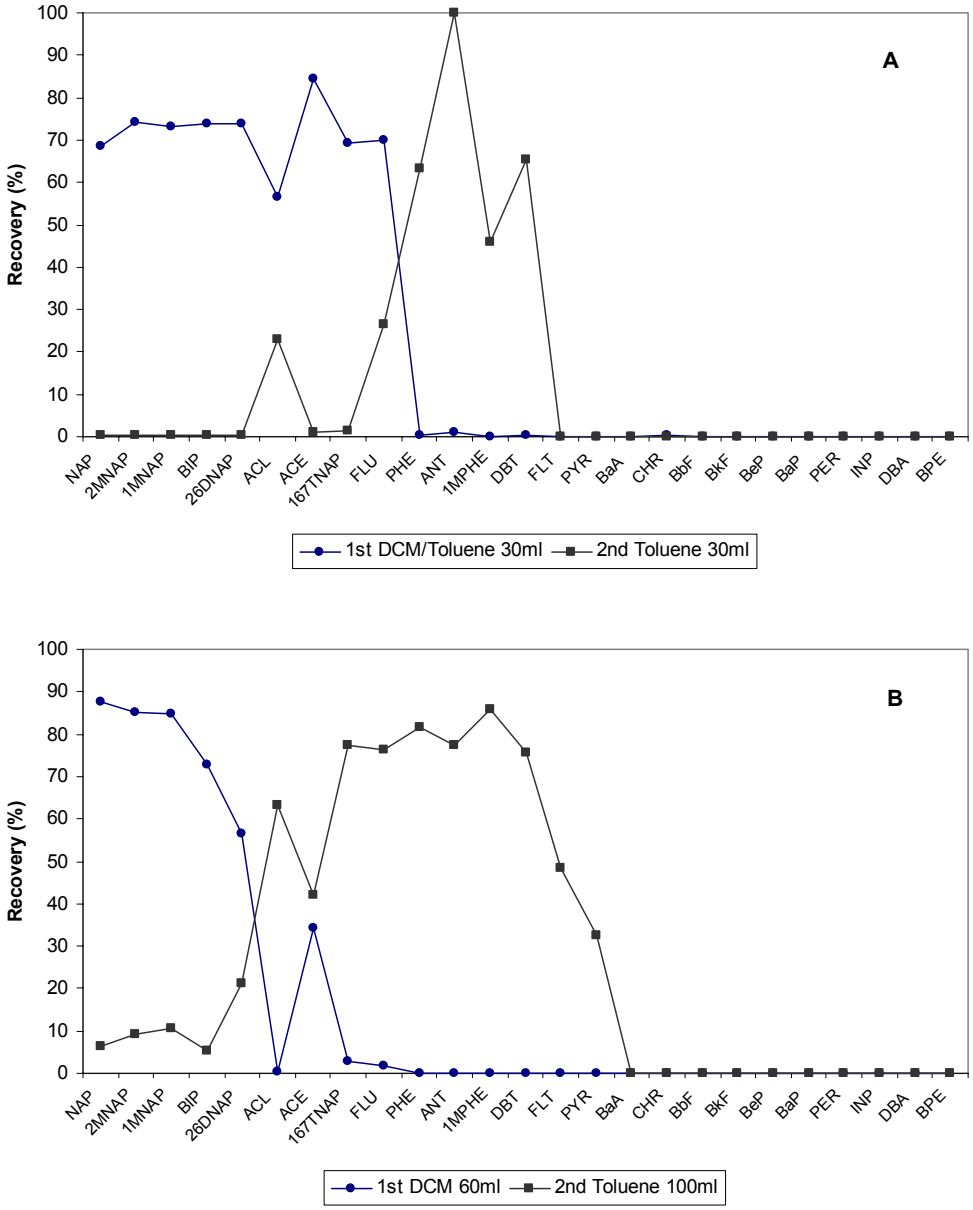


Fig. 4.5. Recoveries of PAH compounds after carbon/silica gel column chromatography. A: Elution with 30 ml dichloromethane (DCM)/toluene and 30 ml of toluene. B: Elution with 60 ml DCM and 100 ml toluene.

column was flipped over and eluted with 60 ml of toluene again. In order to determine how much pentane was needed to attain the separation, a series of carbon column was tested with varying amount of pentane. In the first 40 ml fractions of pentane, no PAH compounds were recovered (recoveries less than 0.1 %). After combining the second and third toluene fractions, the recovery of PAHs was about 74 % on average. High molecular weight PAHs showed relatively good recovery (more than 80 %), while acenaphthylene (57 %) and dibenzothiophene (34 %) had low recoveries (Fig. 4.6).

In addition to the carbon/silica gel column chromatographic techniques, thin layer chromatographic (TLC) techniques were also tested to purify sample extracts after gel permeation chromatography. Five TLC methods were tested (Table 4.1). The separation patterns for each TLC development are illustrated in Fig. 4.7. Among the five development methods, TLC method 1, which uses cyclohexane/toluene 3/2 mixture for development, was selected for purification of samples for isotope analysis. This method had the narrowest PAH band and greatest separation from interferences providing the best purification. The distribution of PAH compounds in each TLC band are shown in Fig. 4.8. The full scan GC/MS chromatograms for each TLC band recovered are shown in Fig. 4.9. This confirmed that all PAH compounds were recovered in band 7 and that there were no PAHs in other bands (band 1 through 6). In an effort to enhance purification, two different development environments, saturated and unsaturated chambers, were tested. The difference in recoveries between the two development environments is shown in Fig. 4.10. Higher recovery rates were observed in the unsaturated chamber developments, especially for low molecular weight PAHs. The difference in recoveries between saturated and unsaturated chambers is in the amount recovered from the upper TLC band above band 7. It seems that solvent-saturated environment expedites the movement of low molecular weight PAHs over high molecular weight PAHs during development. The recovery of PAH compounds in unsaturated TLC separations was about 88 % on average (Fig. 4.10). High molecular weight PAHs had good recoveries (more than 90 %), while low molecular weight PAHs, especially naphthalene, had low recoveries (about 57 %). The low recovery appears to be

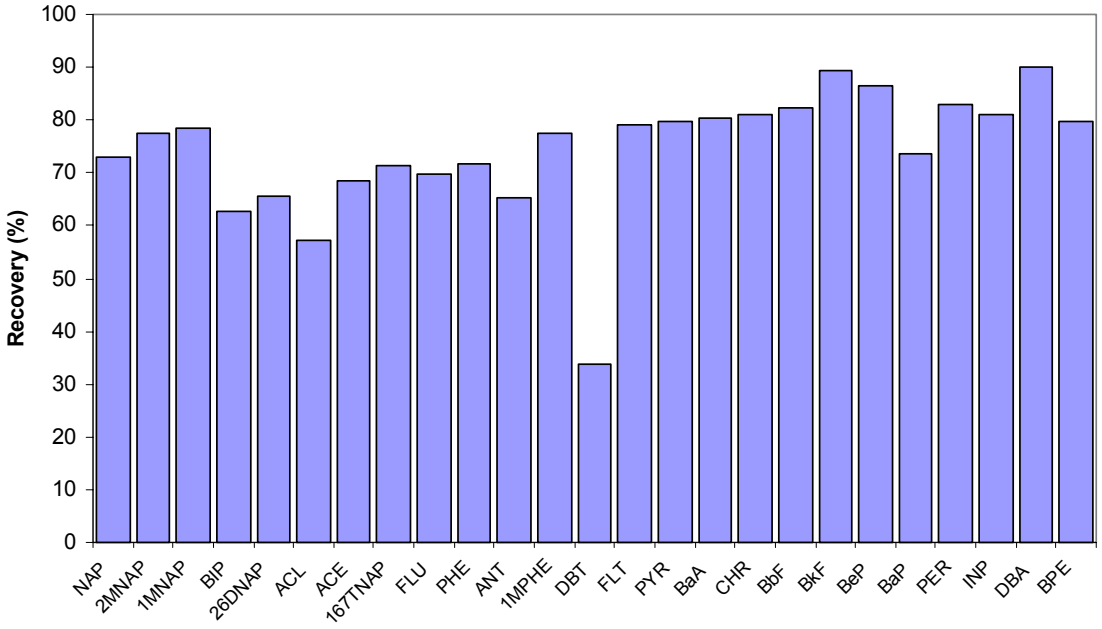


Fig. 4.6. Recoveries of PAH compounds after modified (column reversal) carbon / silica gel column chromatography.

Table 4.1.
Thin layer chromatographic methods tested.

TLC Methods	Plates	Development Solvents	References
1	Silica gel 60 Å	3/2 Cyclohexane/toluene	Modification of Levins (1978)
2	Silica gel 60 Å	3% Acetic acid/hexane	Modification of methods 4
3	Silica gel 60 Å	Dichloromethane	Modification of Lichtfouse *et al*. (1997A)
4	Silica gel 60 Å	Hexane	Modification of Alexander *et al*. (1985)
5	Silver nitrate impregnated silica gel 60 Å	Hexane	Personal correspondence with Robert Kagi

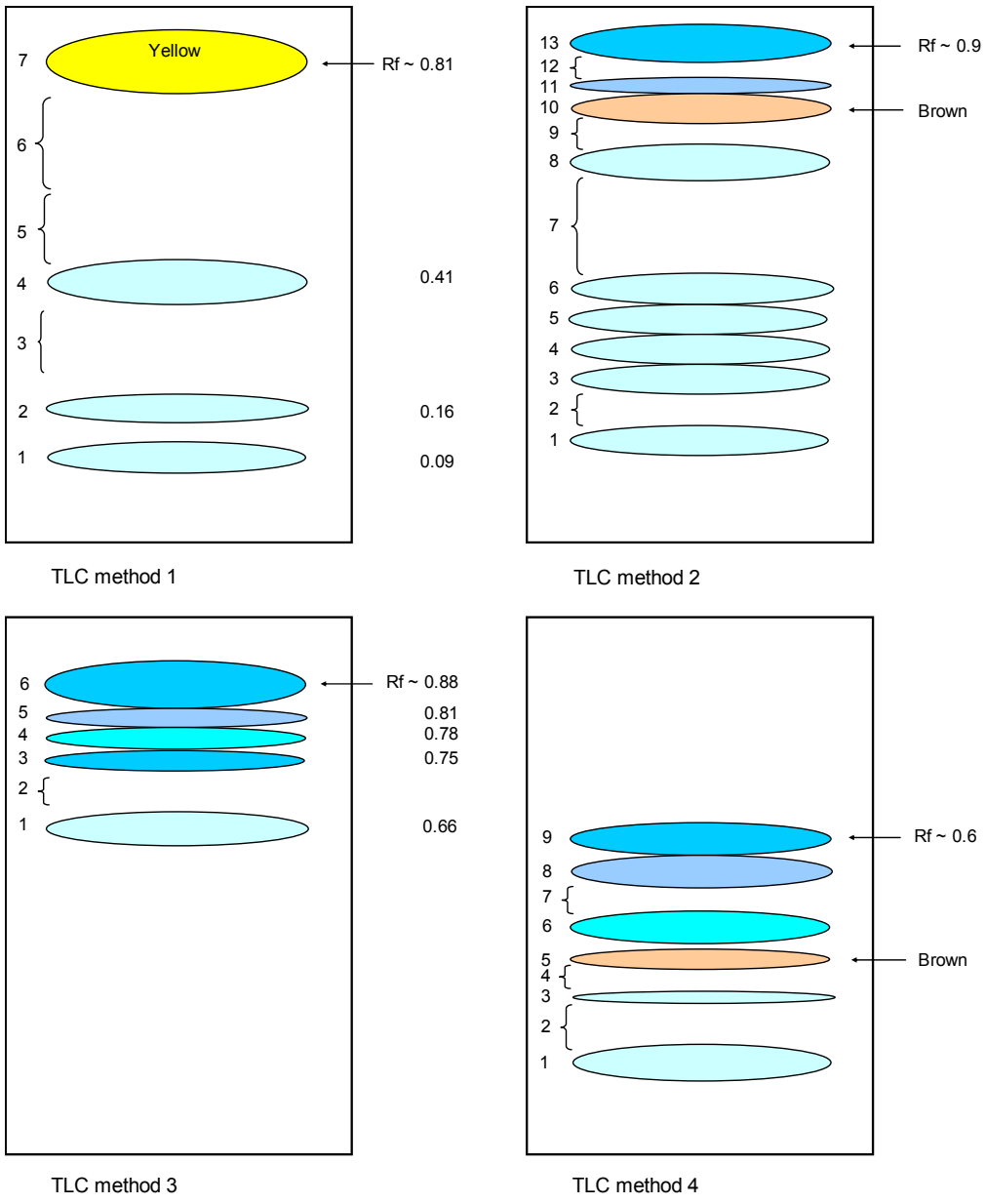


Fig. 4.7. Development patterns of five thin layer chromatographic methods tested.

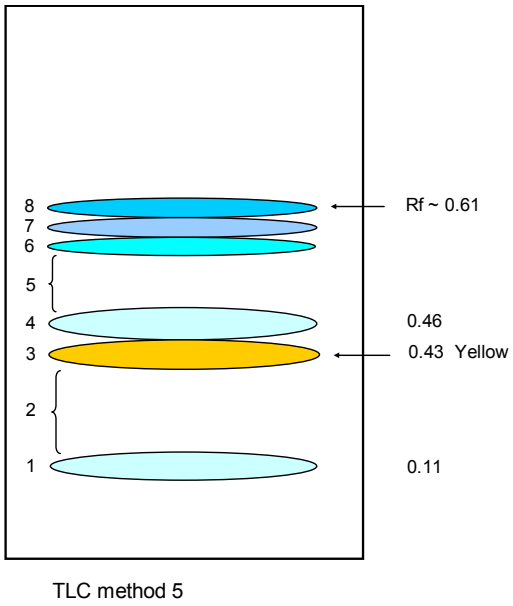


Fig. 4.7. Continued.

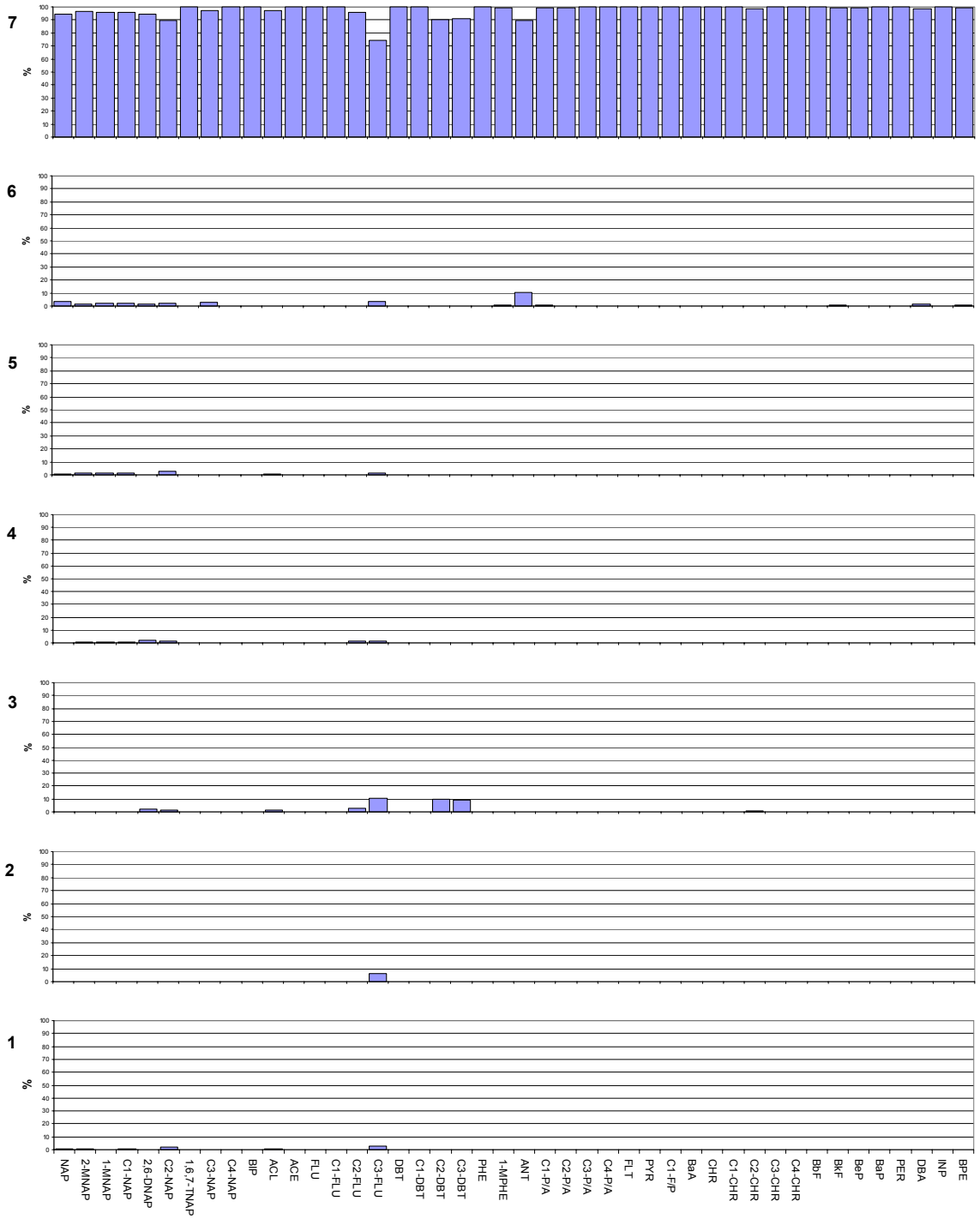


Fig. 4.8. Distribution patterns of PAH compounds in each TLC band (TLC method 1).

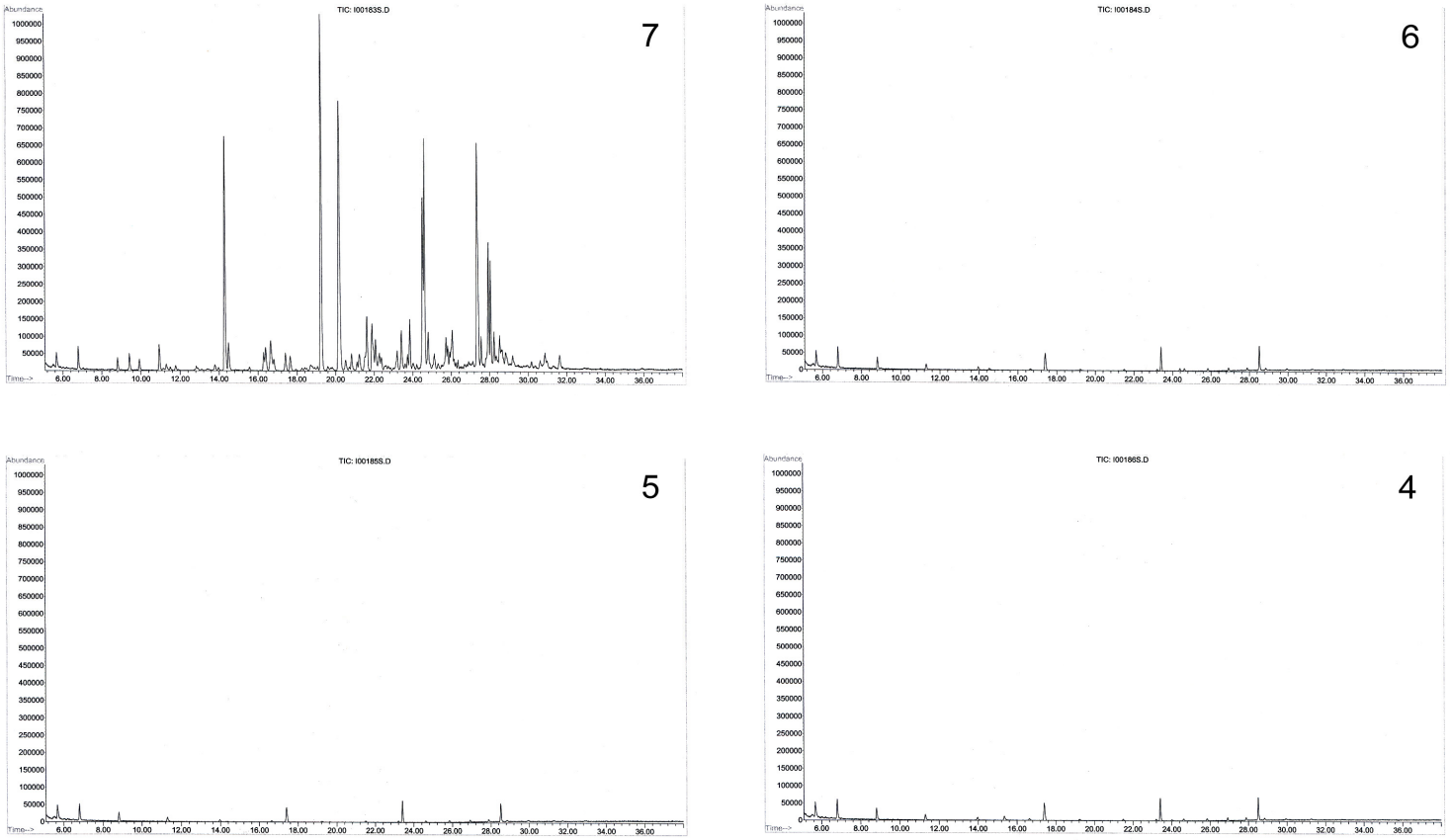


Fig. 4.9. Full scan GC/MS chromatograms for each TLC band recovered from TLC method 1.

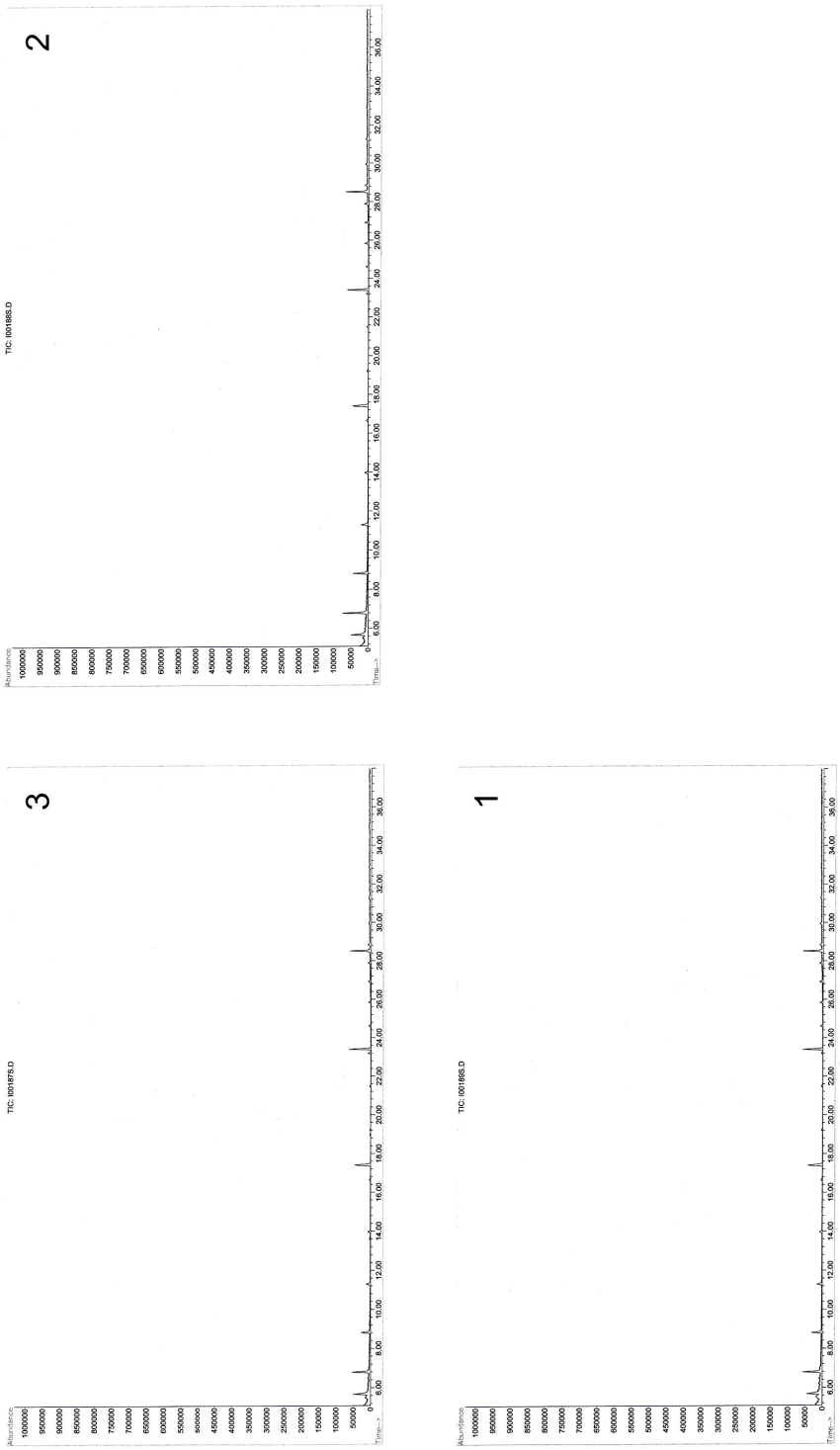


Fig. 4.9. Continued.

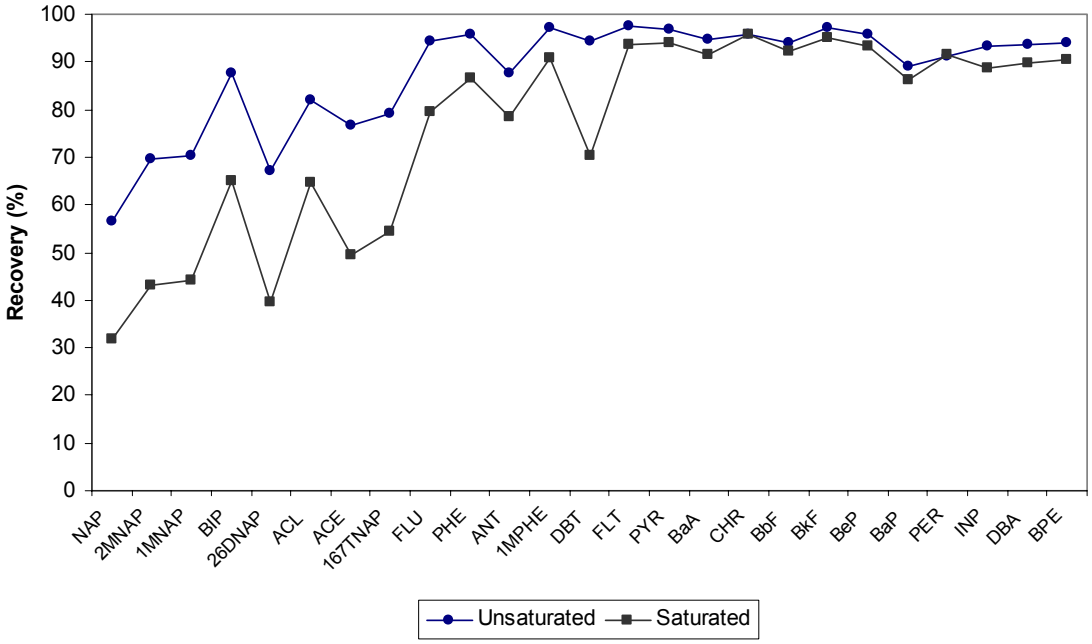


Fig. 4.10. Recoveries of PAH compounds after thin layer chromatography and comparison between saturated and unsaturated chamber environments.

mainly due to evaporative losses of low molecular weight PAHs during the period of solvent (dichloromethane) drying during application of the sample. Evaporative loss of low molecular weight PAHs was confirmed by exposing TLC plate to the air for extended periods of time after sample application. After 30 minutes exposure, recoveries of low molecular weight PAHs were decreased remarkably while no significant differences were observed for high molecular weight PAHs (Fig. 4.11). In order to reduce evaporative losses, application time was minimized and minimal amounts of solvent were used to apply the sample minimizing the time needed to dry the application solvent. In order to accelerate the evaporation of solvent, nitrogen gas was blown across the plate surface. Although nitrogen gas dramatically reduces the drying time, it also accelerates evaporation of low molecular weight PAHs (Fig. 4.11).

The preferred combination of purification methods to process environmental samples for stable carbon isotope ratio analysis is alumina/silica column chromatography, gel permeation chromatography, and thin layer chromatography. Carbon column chromatography can be used after gel permeation chromatography or it can replace the thin layer chromatography if fewer planar impurities, like dioxins or planar PCBs, are present. All extraction, purification, and instrumental techniques were verified by quantitative mass balance of all of the analytes of interest. The recoveries of all PAH compounds after all purification steps are shown in Fig. 4.12. Although there are low recoveries for low molecular weight PAHs, especially for naphthalene (~ 50 %), it is acceptable since there is no isotopic fractionation during purification. Mean recovery for the purification method was ~ 80 %. The purity of isolates was confirmed by gas chromatography with flame ionization detection and full scan mass spectrometry. The full scan mass fragmentogram of sample after each purification step are shown in Fig. 4.13. It is clear that peak resolution is improved and that the baseline, which is mostly the unresolved complex mixture, is decreased after each purification step. The mass spectra of selected PAH compounds from a sample and the reference spectra from NIST (National Institute of Standards and Technology) mass spectral data base are shown in Fig. 4.14. The mass spectra of sample components are similar to the reference spectra

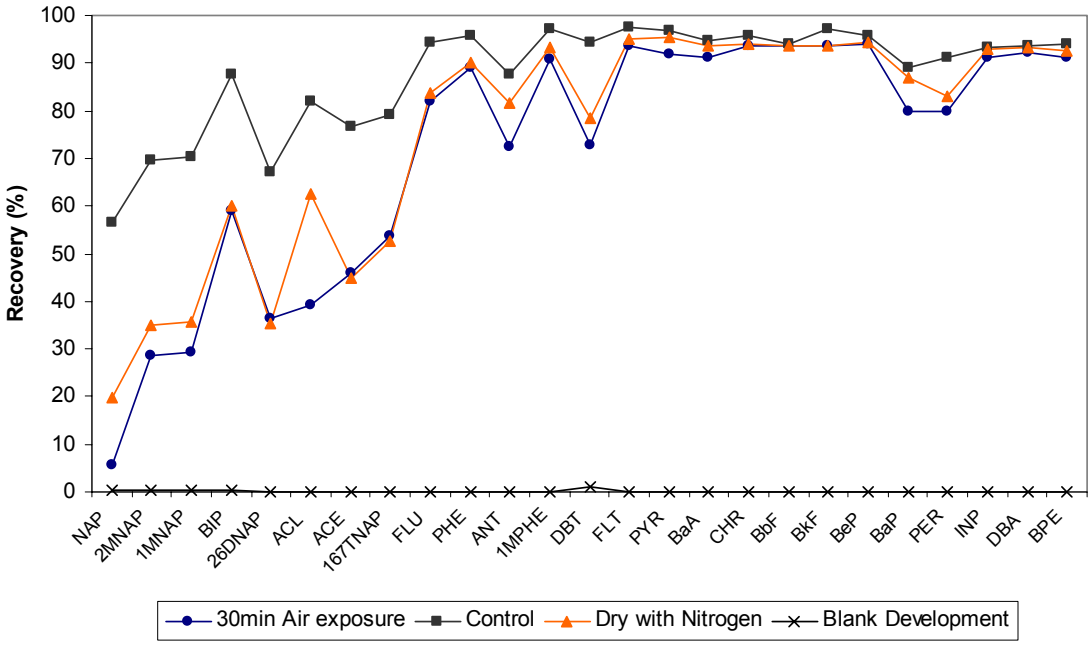


Fig. 4.11. Recoveries of PAH compounds after thin layer chromatography under different development conditions in unsaturated chamber.

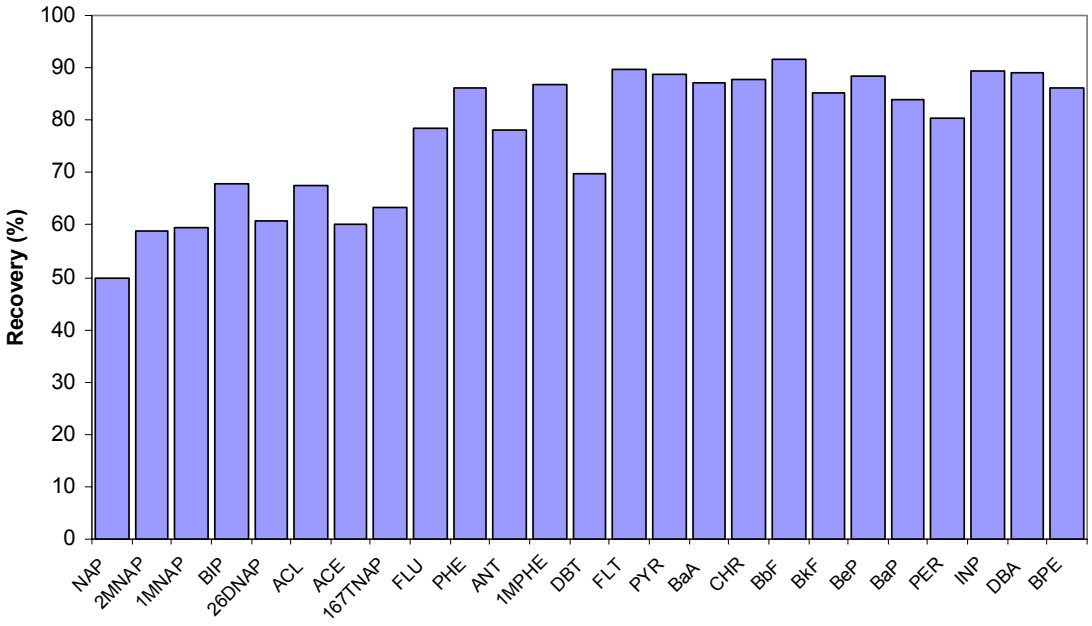


Fig. 4.12. Recoveries of PAH compounds after all purification steps including alumina/silica gel column chromatography, gel permeation chromatography, and thin layer chromatography.

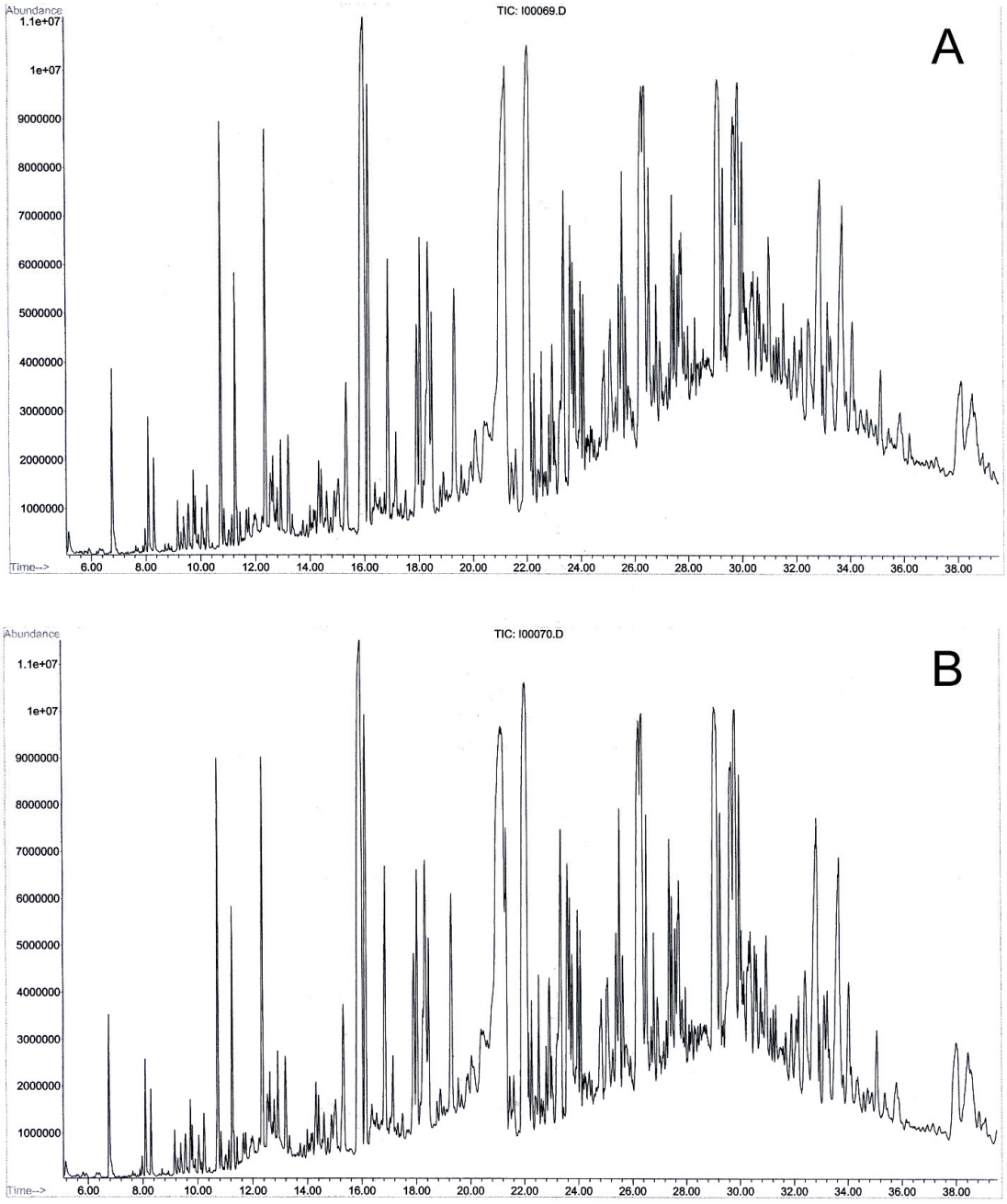


Fig. 4.13. Full scan GC/MS chromatograms of sediment sample after each purification step. A: After Al/Si column chromatography, B: after GPC, C: after carbon/silica gel column chromatography, D: after TLC.

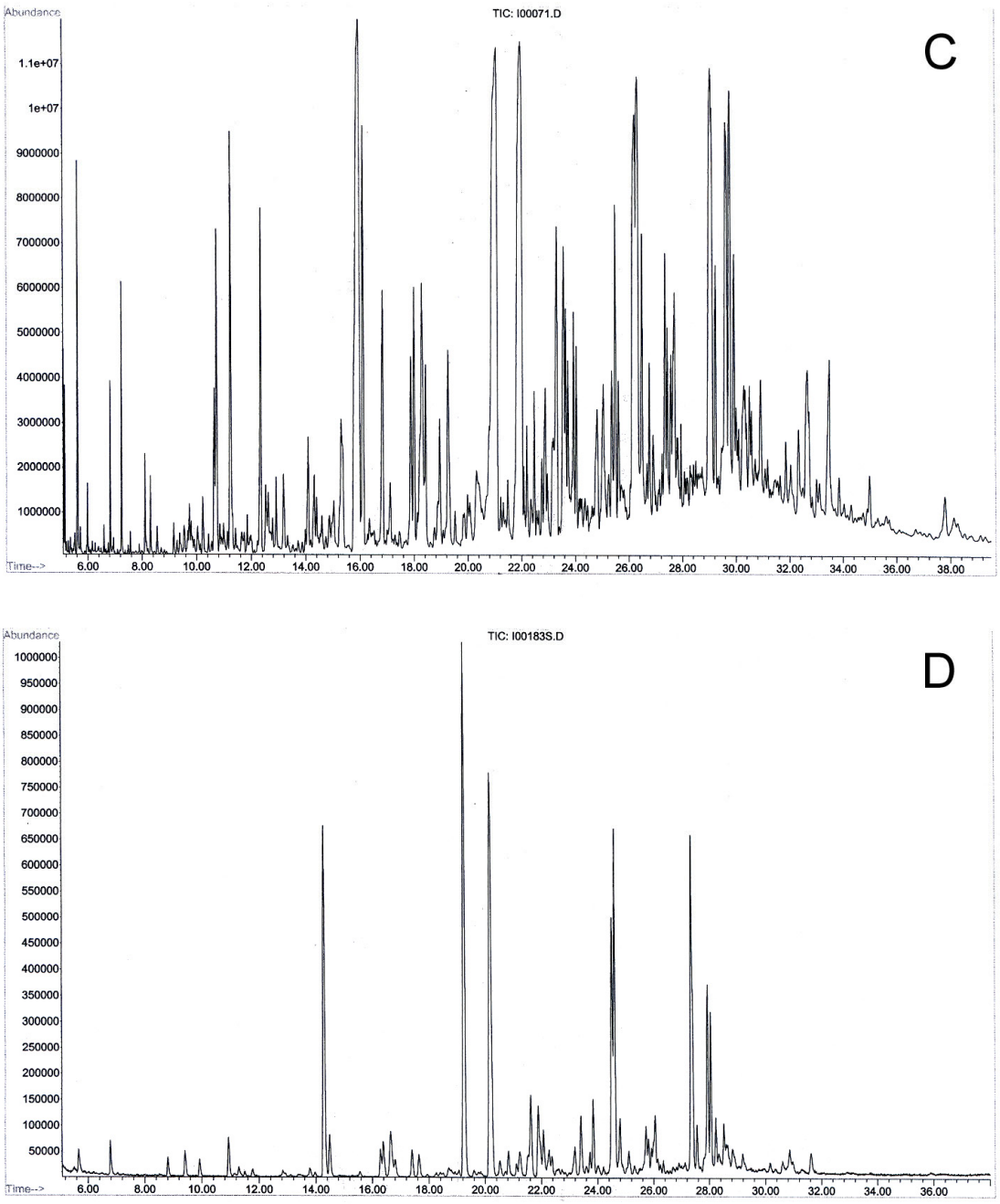


Fig. 4.13. Continued.

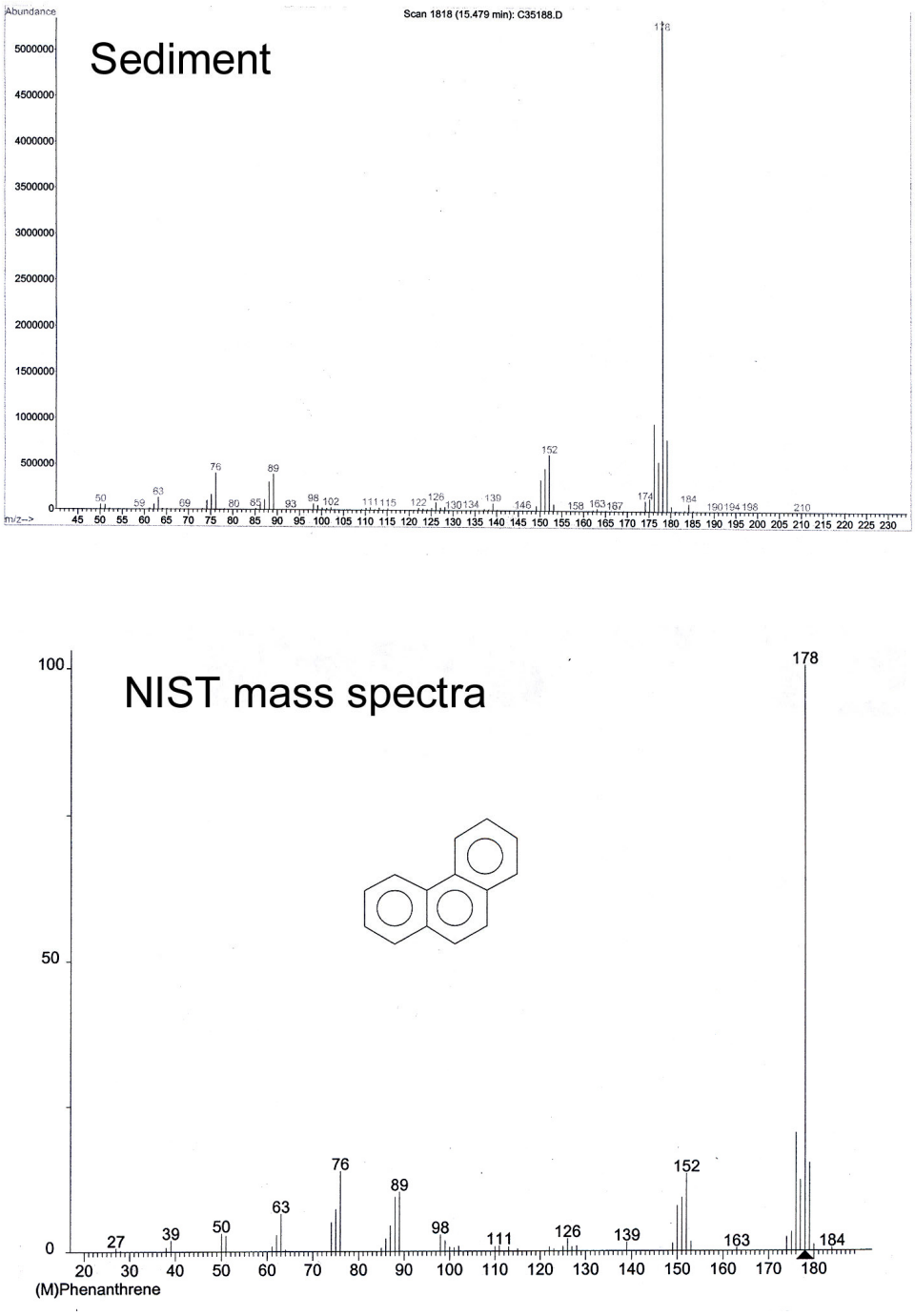
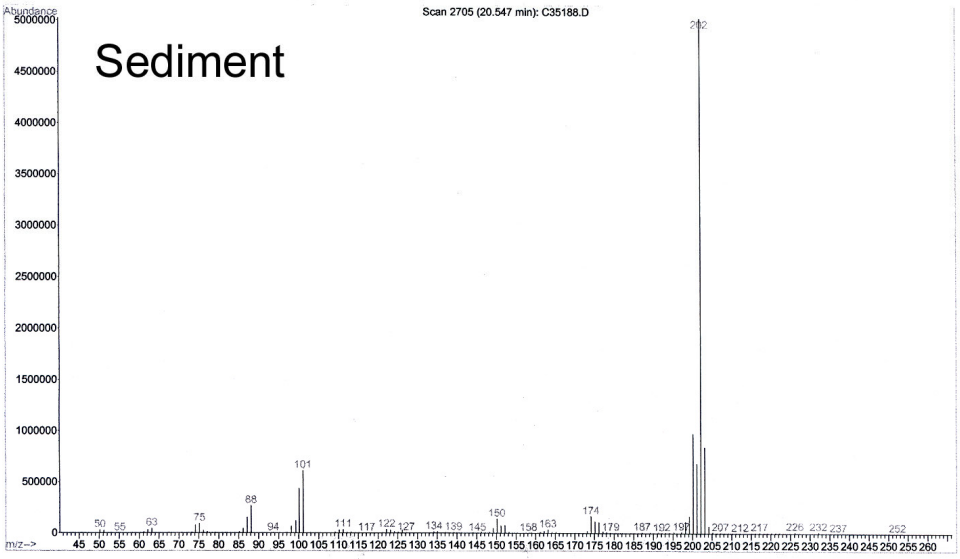


Fig. 4.14. Mass spectra of selected PAH compounds in a sediment sample after purification and their reference spectra from NIST mass spectral data base (phenanthrene).



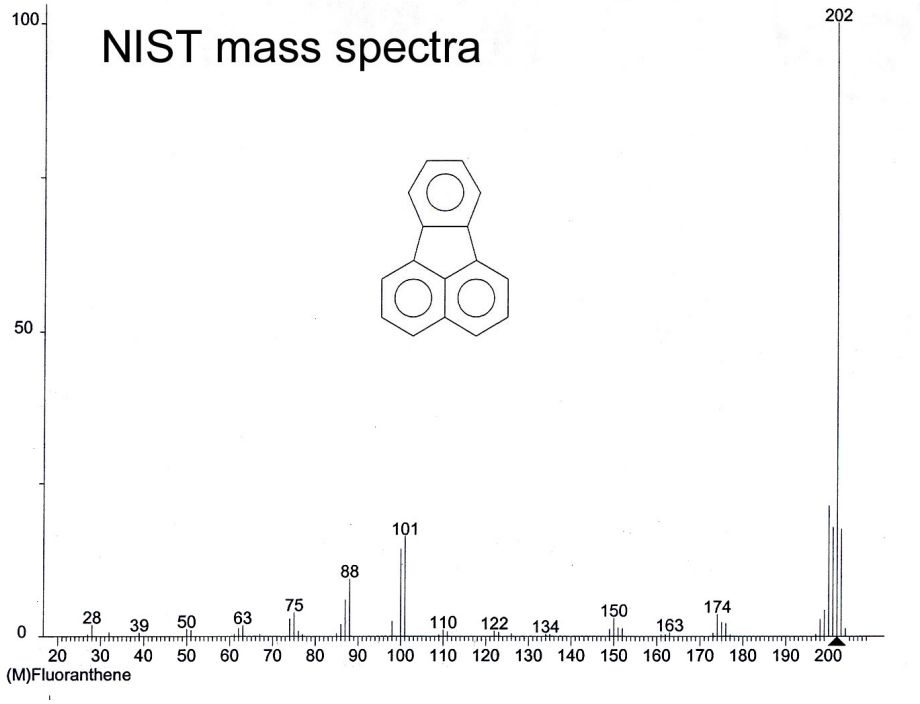


Fig. 4.14. Continued (fluoranthene).

and show few interfering ions (93 % and 95 % match qualities for phenanthrene and fluoranthene, respectively). GC/FID analysis of samples after purification is shown in Fig. 4.15 confirming that the peaks are well resolved and that the baseline is low.

A Finnigan MAT 252 isotope ratio mass spectrometer was coupled to a Varian 3400 gas chromatograph via a combustion interface. Initial GC conditions were the same as used for PAH quantification. To increase analyte response and remove solvent tailing, sample were injected in a splitless mode and the inlet was purged for 2 minutes. Under these GC condition, long solvent tails were produced that interfere with the analysis of PAHs. In order to minimize solvent tailing in Varian GC system, the inlet purge time was adjusted. The response of selected peaks in terms of peak height and area according to their purge time is summarized in Fig. 4.16. More than 90 % of the detector response occurred within 50 seconds and, after 1 minute, no increase was observed. Therefore the analyte can be introduced onto the column within 50 seconds after injection with 10 % of the analyte purged out of the injection port. Thus the solvent tail can be easily removed because it usually account for less than 5 % of total detector response as shown in Fig. 4.17 (Matthew, 1991). The splitless time was adjusted to 50 seconds.

The combustion furnace, a water removal system and an open split in GC/IRMS system resulted in potential analytical problems. Differing internal and external diameters of tubing and their connectors, created dead volume which causes tailing of individual peaks. Dead volume is created at any point in the carrier gas flow path where the diameter in the path increases. As the sample encounters dead volume along the flow path, the back pressure on the sample decreases and flow slows as the carrier gas and sample expands into the additional space available. Dead volumes can severely affect the results of the isotope measurements due to broad peaks and peak tailing. Peak resolution is essential for accurate compound specific isotope analysis (Meier-Augenstein, 1997; Ellis and Fincannon, 1998). In order to improve peak resolution by narrowing the peak width, the injection port head pressure was adjusted. Higher gas chromatograph head pressures created faster column gas flows resulting in narrower peak shapes (Lee *et al*., 1984; Ellis and Fincannon, 1998). GC/IRMS chromatographic traces of standard

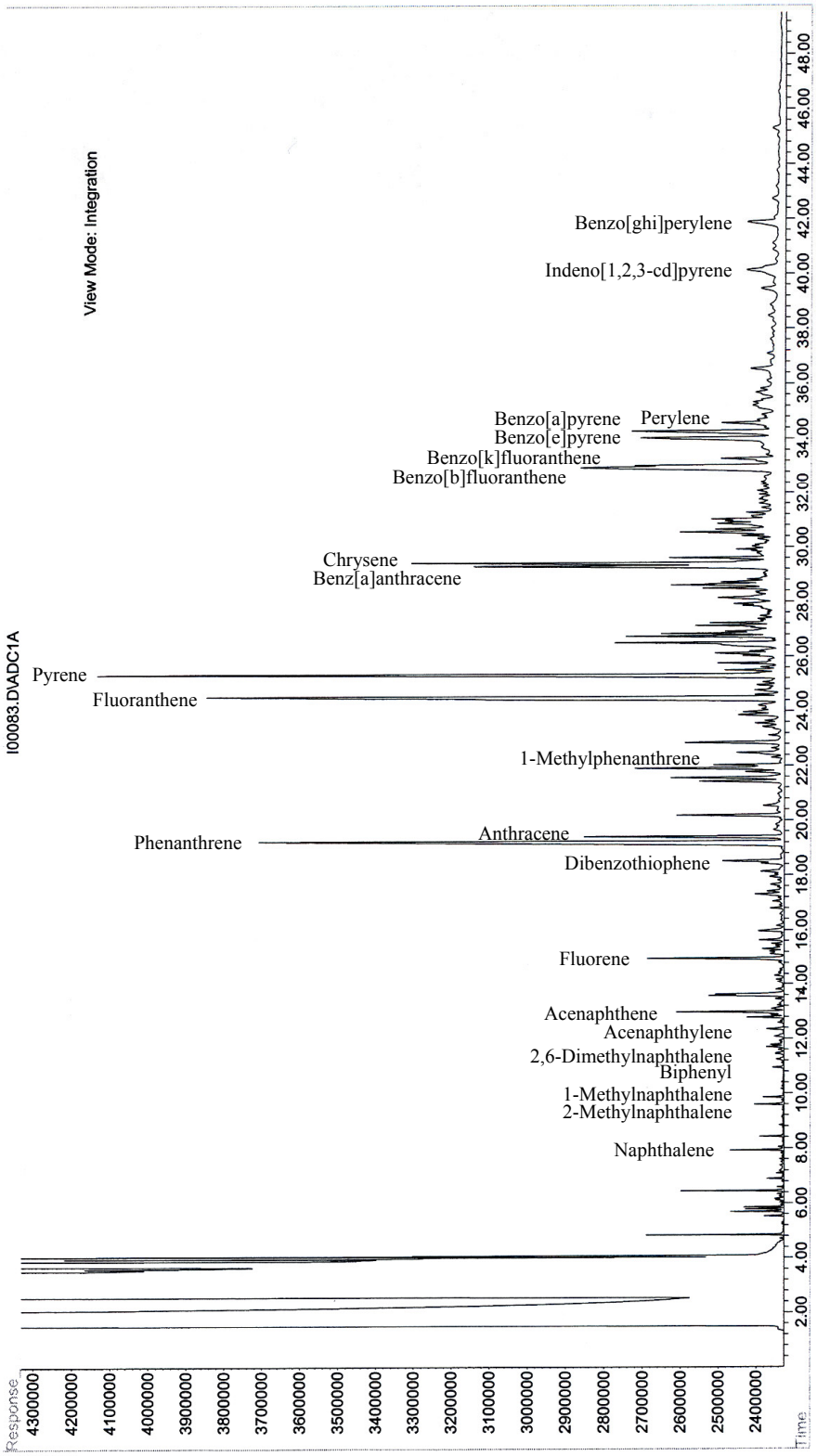


Fig. 4.15. GC/FID chromatogram of a sediment sample after purification.

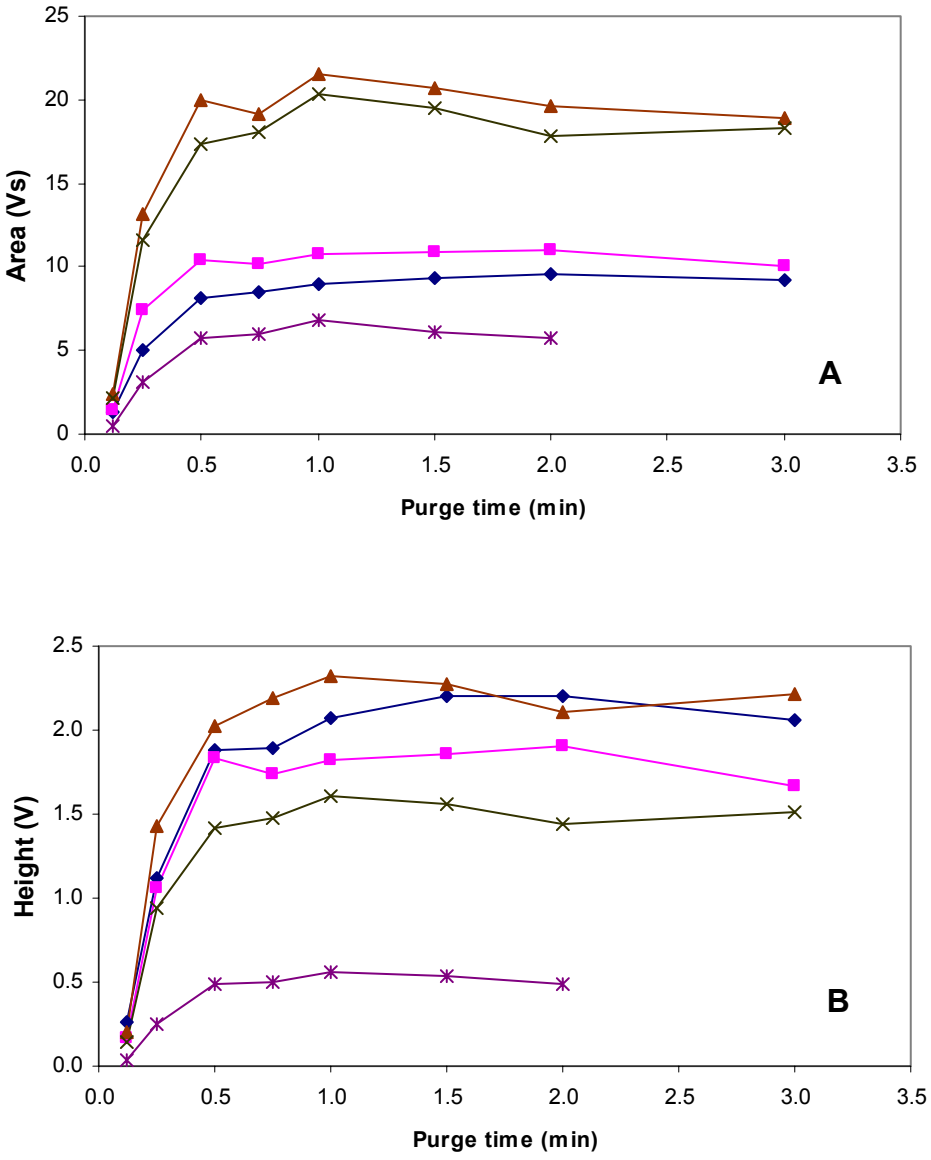


Fig. 4.16. Responses of selected peaks according to the change of inlet purge time. (A: Area, B: height).

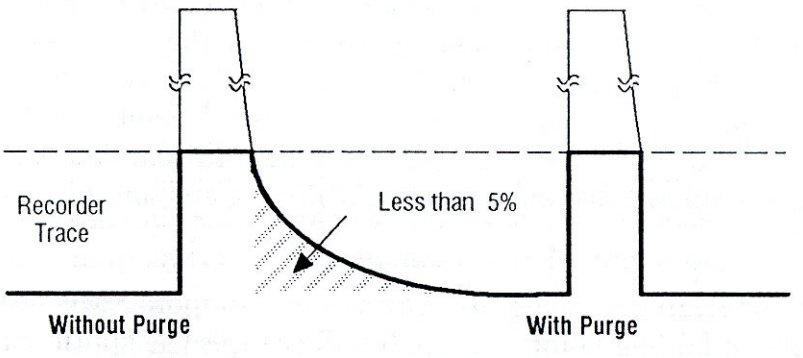


Fig. 4.17. Influence of inlet purge on solvent peak.

materials and selected sediment extracts are shown in Fig. 4.18. A head pressure of 30 psi was enough to narrow peak shape.

Some closely eluting PAH peaks (Fig. 4.19) could not be resolved to baseline-separation. In this case, peak areas and isotope ratios were combined using the following isotope balance equation.

$$\delta^{13}C_{A\&B} = \left(a_A\delta^{13}C_A + a_B\delta^{13}C_B\right)/\left(a_A + a_B\right)$$

where a_A and a_B is the area of the peak A and B, $\delta^{13}C_A$ and $\delta^{13}C_B$ are the stable carbon isotope ratio of the peak A and B, respectively (Boschker *et al*., 1999; Jones, 2001).

Before analysis, the instrument was routinely tested for the performance. Peak resolution between mass 44 and 45 peaks must be more than 200 at 10 % of the valley. Peak resolution is determined by dividing the peak distance between two neighboring peaks by the peak width of m/z 44. This performance check also tested signal linearity of the isotope ratios versus the beam intensity of m/z 44. An example of result of the linearity calibrations are shown in Table 4.2. Once the linearity range was identified, peak heights in actual samples were adjusted to be within the linearity range by dilution or concentration of the samples. This was facilitated by using the concentration data obtained by GC/MS/SIM analysis. In addition to peak resolution and linearity checks, the instrument was routinely tested for system and signal stability, sensitivity, and peak flatness as per the instrument manual. Peak centering was performed whenever samples were injected before the triple introduction of standard gas. Correction for background carbon dioxide eluted during GC/IRMS analysis was also made automatically by ISODAT acquisition software.

The precision of the stable carbon isotope analysis was verified by repeated processing and injection of authentic standards and samples. Stable carbon isotope values for multiple injections of standard reference materials are shown in Table 4.3. For all measured individual compounds or combined peaks, the standard deviation for multiple analyses ranged between 0.08 and 0.43 ‰. The relationship between peak area and the standard deviation for multiple isotope measurements is shown in Fig. 4.20. From the figure, it is clear that precision of the measurement increases with peak size

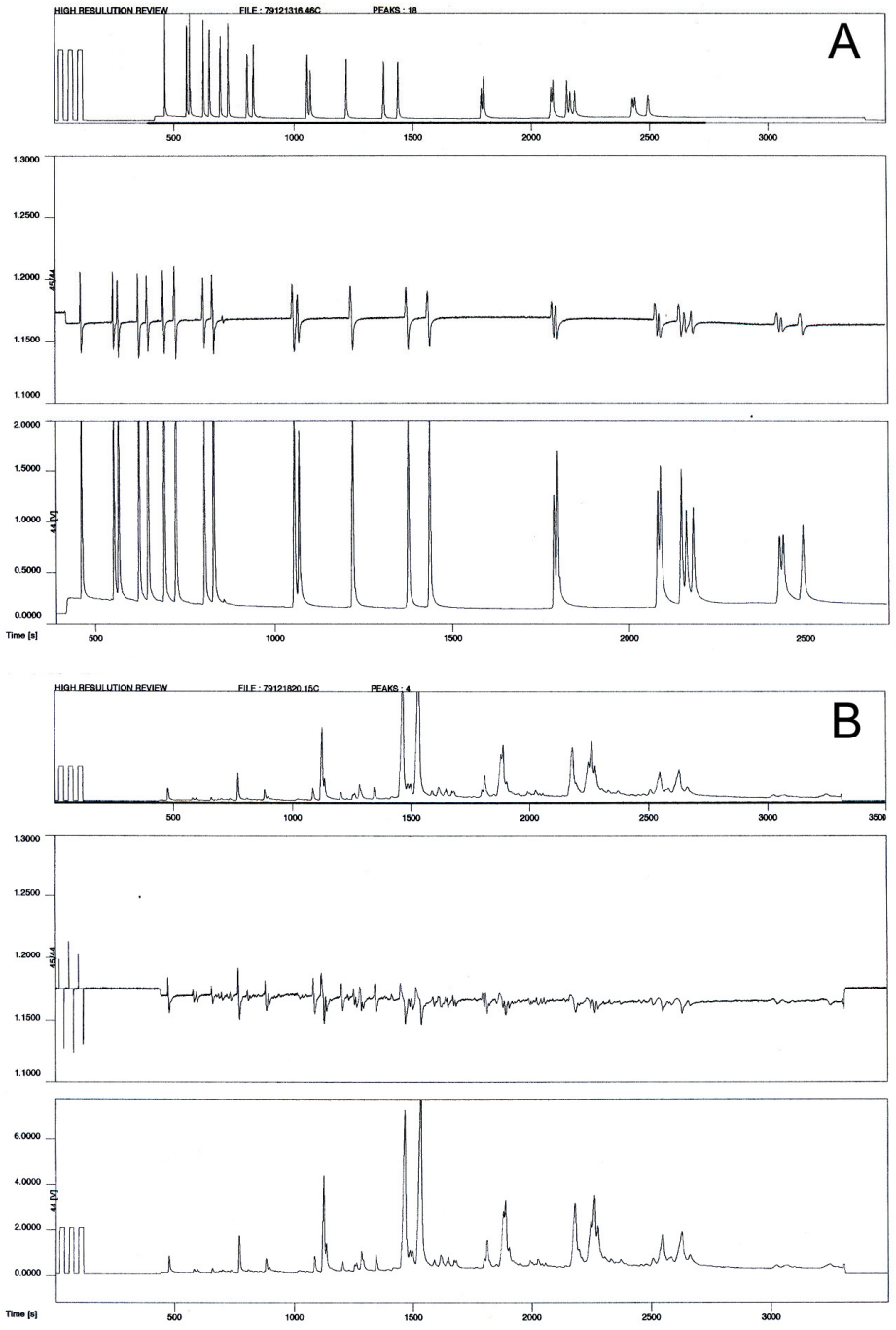


Fig. 4.18. GC/IRMS chromatographic traces (m/z 44) of standard material (A) and selected sample (B) along with their m/z 45/44 ratio traces.

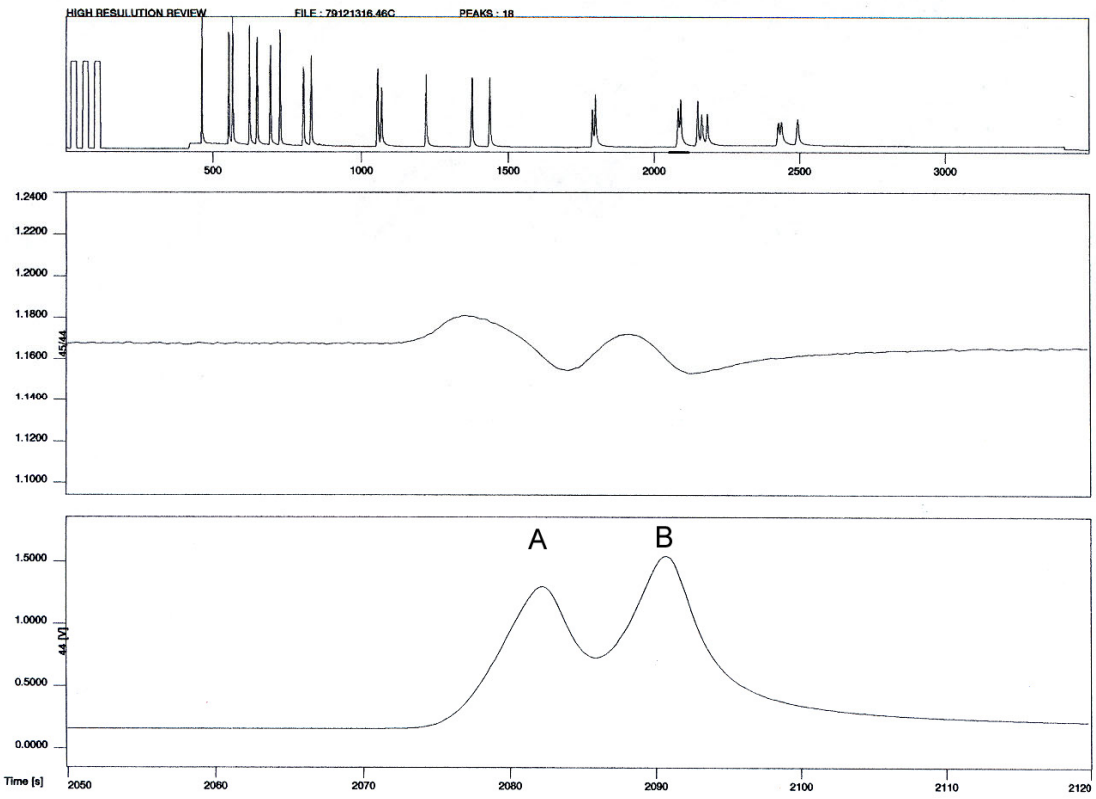


Fig. 4.19. GC/IRMS chromatogram of close eluting peaks A (benzo[b]fluoranthene) and B (benzo[k]fluoranthene).

Table 4.2.
Example of result of the linearity calibration and the evaluation.

	44 [V]	45/44	46/44	45 [‰]	46[‰]
1:	1.90620	1.14919	1.40855	0.00000	0.00000
2:	2.98267	1.14921	1.40871	0.01843	0.10979
3:	4.05237	1.14920	1.40869	0.00924	0.09799
4:	4.96302	1.14918	1.40880	-0.00928	0.17717
5:	6.01696	1.14906	1.40868	-0.11492	0.08879
6:	6.98864	1.14907	1.40864	-0.10378	0.05783
SLOPE :		-0.00003	0.00001	-0.02631	0.00882
INTERC.:		1.14929	1.40862	0.08463	0.04904
SYSTEM BASELINE 44:			0.09863		
SYSTEM BASELINE 45:			0.09838		
SYSTEM BASELINE 46:			0.09898		

Table 4.3.
Stable carbon isotope ratios of standard reference material (SRM 2260).

Peak No.	Compounds	Run 1	Run 2	Run 3	Run 4	Avg.	SD
				$\delta^{13}C$			
1	**Naphthalene**	-23.40	-23.09	-23.68	-23.85	-23.51	0.33
2	**2-Methylnaphthalene**	-20.78	-20.87	-21.01	-21.34	-21.00	0.25
3	**1-Methylnaphthalene**	-26.99	-26.80	-27.12	-27.13	-27.01	0.15
4	**2+3**	-25.00	-24.87	-25.07	-25.18	-25.03	0.13
5	**Biphenyl**	-26.34	-26.46	-26.52	-26.68	-26.50	0.14
6	**2,6-Dimethylnaphthalene**	-21.87	-22.32	-22.22	-22.52	-22.23	0.27
7	**Acenaphthylene**	-21.59	-21.84	-21.64	-21.85	-21.73	0.13
8	**Acenaphthene**	-22.56	-22.66	-22.83	-22.61	-22.67	0.12
9	**1,6,7-Trimethylnaphthalene**	-20.35	-20.59	-20.81	-20.58	-20.58	0.19
10	**Fluorene**	-23.13	-22.87	-23.82	-23.41	-23.31	0.41
11	**Phenanthrene**	-23.65	-23.78	-23.77	-23.40	-23.65	0.18
12	**Anthracene**	-24.00	-23.80	-23.70	-23.75	-23.81	0.13
13	**11+12**	-23.83	-23.93	-23.93	-23.65	-23.84	0.13
14	**1-Methylphenanthrene**	-24.07	-24.12	-23.78	-23.53	-23.88	0.27
15	**Fluoranthene**	-24.40	-24.43	-23.83	-23.57	-24.06	0.43
16	**Pyrene**	-23.78	-24.19	-23.66	-23.30	-23.73	0.37
17	**Benz[a]anthracene**	-22.43	-22.24	-22.20	-22.08	-22.24	0.15
18	**Chrysene**	-23.98	-24.08	-24.20	-24.02	-24.07	0.10
19	**17+18**	-23.05	-23.61	-23.70	-23.46	-23.46	0.29
20	**Benzo[b]fluoranthene**	-20.81	-21.14	-20.97	-20.75	-20.92	0.17
21	**Benzo[k]fluoranthene**	-25.23	-25.43	-25.29	-25.20	-25.29	0.10
22	**20+21**	-23.86	-24.12	-23.96	-23.78	-23.93	0.15
23	**Benzo[e]pyrene**	-21.70	-21.37	-21.75	-21.70	-21.63	0.17
24	**Benzo[a]pyrene**	-23.78	-23.85	-23.97	-23.86	-23.87	0.08
25	**Perylene**	-24.41	-24.38	-24.71	-24.63	-24.53	0.16
26	**23+24+25**	-23.37	-23.31	-23.58	-23.49	-23.44	0.12
27	**Indeno[1,2,3-cd]pyrene**	-21.51	-21.30	-21.19	-21.31	-21.33	0.13
28	**Dibenz[a,h]anthracene**	-24.46	-24.70	-24.10	-24.57	-24.46	0.26
29	**27+28**	-23.25	-23.59	-23.21	-23.42	-23.37	0.17
30	**Benzo[ghi]perylene**	-23.06	-23.02	-23.21	-23.25	-23.14	0.11

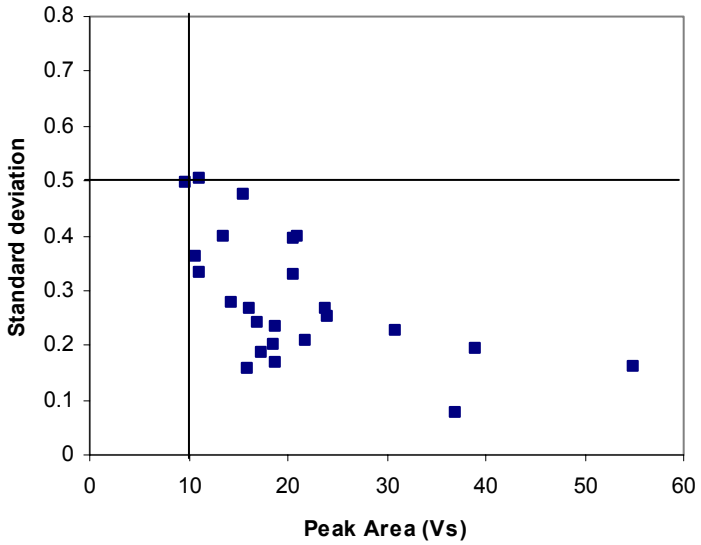


Fig. 4.20. Relationship of peak area and standard deviation of multiple isotope measurements.

mainly because the smaller the peaks are, the greater the contribution from background or interfering materials. For the precise analysis of stable carbon isotope ratio, peaks greater than 10 Vs in peak area were used. The result of multiple injections of environmental sample after purification is shown in Table 4.4. The standard deviations in isotope ratios for multiple injection fall in the range of 0.13 ~ 0.73 ‰. This is compared with the result from other literature values in Table 4.4. The analytical protocol developed provides similar or more precise isotope ratio data than other analytical methods in the literature.

The use of internal standards with known isotopic compositions provides further verification of instrumental performance. Excellent accuracy can be achieved by introducing standard material of known isotopic composition and determine the isotopic ratio of individual compounds in the sample and comparing it to the standard. Standard CO_2 gas was introduced in triplicate at the beginning of each run by means of an open split and subjected to the same condition as the samples.

The analytical protocols were evaluated to ensure that compositional and stable isotopic integrity is preserved throughout the analytical protocol by processing analyte standards of known stable isotopic composition. The results of stable carbon isotopic measurements of standard materials after purification are summarized in Table 4.5. These values are compared with those of unprocessed standard materials in Fig. 4.21. A diagonal line represents a 1:1 ratio between the isotope values of processed and unprocessed standard materials. Most compounds show a linear relationship and isotopic conservation during the purification processes, although some analytes show a slight isotopic enrichment during purification. Enrichment may be caused by isotopic fractionation during the concentration steps due to evaporation causing a preferential loss of isotopically light PAH compounds. However all of the measured isotope ratios for purified standards fall within two standard deviation (2σ) of the mean isotope ratio of unprocessed standard material. One exception is the combined peaks of benzo[e]pyrene, benzo[a]pyrene, and perylene, which may require a correction factor of – 0.4 ‰ (Fig. 4.22).

Table 4.4.
Standard deviations of stable carbon isotope ratios of PAHs in a selected sediment sample and comparison with other literature values.

	Current Study 2004	Yanik *et al* 2003	Ballentine *et al* 1996	O'Malley *et al* 1997	
	Sediment	Sediment	Aerosol	Aerosol	Standard
Total range	0.13-0.73	0.43-1.21	0.2-0.8	0.15-0.65	0.15-0.40
Naphthalene	0.47			0.25-0.40	
2-Methylnaphthalene	0.36	0.54		0.25-0.45	
1-Methylnaphthalene	0.46				
Biphenyl	0.56				
2,6-Dimethylnaphthalene	0.52	0.90-1.21		0.25-0.35	
Acenaphthylene	0.73			0.35	
Acenaphthene	0.33			0.15-0.20	
1,6,7-Trimethylnaphthalene		0.43-1.15			
Fluorene	0.44			0.20-0.65	
Phenanthrene (PHE)	0.36		0.20	0.35-0.45	
Anthracene (ANT)	0.13				
PHE+ANT	0.56				
1-Methylphenanthrene	0.26	0.84		0.20-0.50	
Fluoranthene	0.44		0.80	0.30	
Pyrene	0.45		0.80	0.40	
Benz[a]anthracene (BaA)	0.40				
Chrysene (CHR)	0.55				
BaA+CHR	0.69				
Benzo[b+k]fluoranthene	0.30				
Benzo[e]pyrene	0.45				
Benzo[a]pyrene	0.32				
Perylene	0.49				
INP+DBA*	0.55				
Benzo[ghi]perylene	0.41				

*** INP: indeno[1,2,3-cd]pyrene, DBA: dibenz[a,h]anthracene.**

Table 4.5.
Stable carbon isotope ratios of standard reference material (SRM 2260) after purification processes.

Peak No.	Compounds	Run 1	Run 2	Run 3	Avg.	SD
		$\delta^{13}C$				
1	**Naphthalene**	-23.00	-23.28	-23.73	-23.34	0.37
2	**2-Methylnaphthalene**	-19.93	-20.76	-20.74	-20.48	0.47
3	**1-Methylnaphthalene**	-26.56	-27.01	-27.41	-26.99	0.43
4	**2+3**	-24.34	-24.77	-25.03	-24.71	0.35
5	**Biphenyl**	-25.90	-26.17	-26.28	-26.12	0.20
6	**2,6-Dimethylnaphthalene**	-22.44	-22.02	-22.11	-22.19	0.22
7	**Acenaphthylene**	-21.86	-21.43	-21.49	-21.59	0.23
8	**Acenaphthene**	-22.45	-22.63	-22.33	-22.47	0.15
9	**1,6,7-Trimethylnaphthalene**	-20.29	-20.22	-20.06	-20.19	0.12
10	**Fluorene**	-22.61	-23.22	-23.05	-22.96	0.31
11	**Phenanthrene**	-23.38	-23.93	-23.91	-23.74	0.31
12	**Anthracene**	-23.32	-24.09	-24.21	-23.87	0.48
13	**11+12**	-23.54	-24.00	-24.04	-23.86	0.28
14	**1-Methylphenanthrene**	-23.25	-23.53	-23.37	-23.38	0.14
15	**Fluoranthene**	-23.52	-23.35	-23.66	-23.51	0.16
16	**Pyrene**	-23.24	-23.00	-23.20	-23.15	0.13
17	**Benz[a]anthracene**	-22.38	-21.75	-22.14	-22.09	0.32
18	**Chrysene**	-24.24	-23.54	-23.92	-23.90	0.35
19	**17+18**	-23.68	-23.03	-23.40	-23.37	0.33
20	**Benzo[b]fluoranthene**	-20.64	-20.49	-20.61	-20.58	0.08
21	**Benzo[k]fluoranthene**	-25.33	-25.16	-25.40	-25.30	0.12
22	**20+21**	-23.81	-23.87	-23.81	-23.83	0.03
23	**Benzo[e]pyrene**	-21.20	-21.17	-21.19	-21.19	0.02
24	**Benzo[a]pyrene**	-23.36	-23.55	-23.54	-23.48	0.11
25	**Perylene**	-23.81	-23.86	-24.24	-23.97	0.24
26	**23+24+25**	-22.96	-22.90	-23.01	-22.96	0.06
27	**Indeno[1,2,3-cd]pyrene**	-20.41	-20.61	-20.76	-20.59	0.18
28	**Dibenz[a,h]anthracene**	-24.18	-24.23	-24.48	-24.30	0.16
29	**27+28**	-22.91	-22.99	-23.21	-23.04	0.16
30	**Benzo[ghi]perylene**	-22.82	-23.40	-23.24	-23.15	0.30

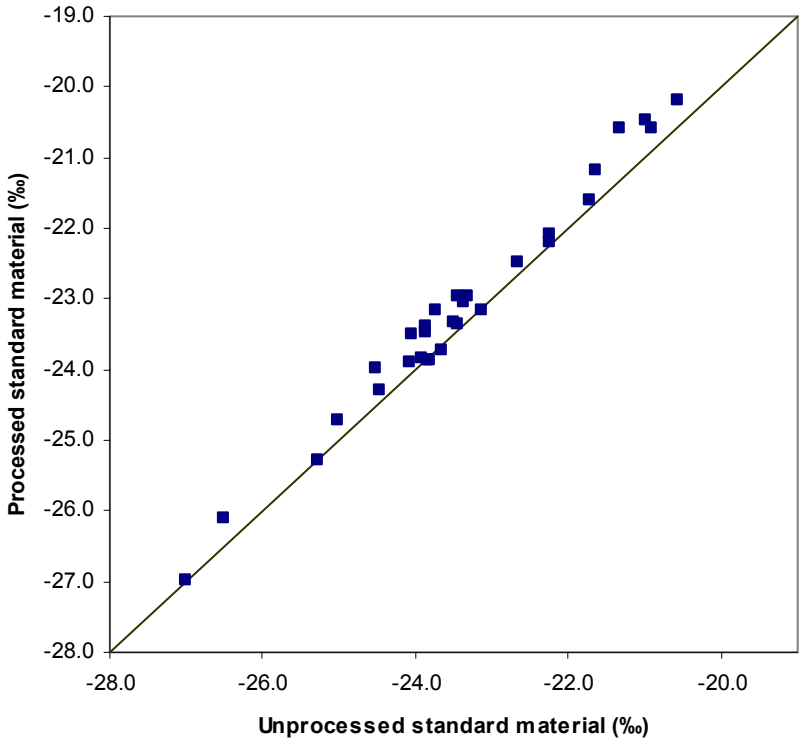


Fig. 4.21. Relationship of stable carbon isotope ratios of PAHs between processed standard material and unprocessed standard material.

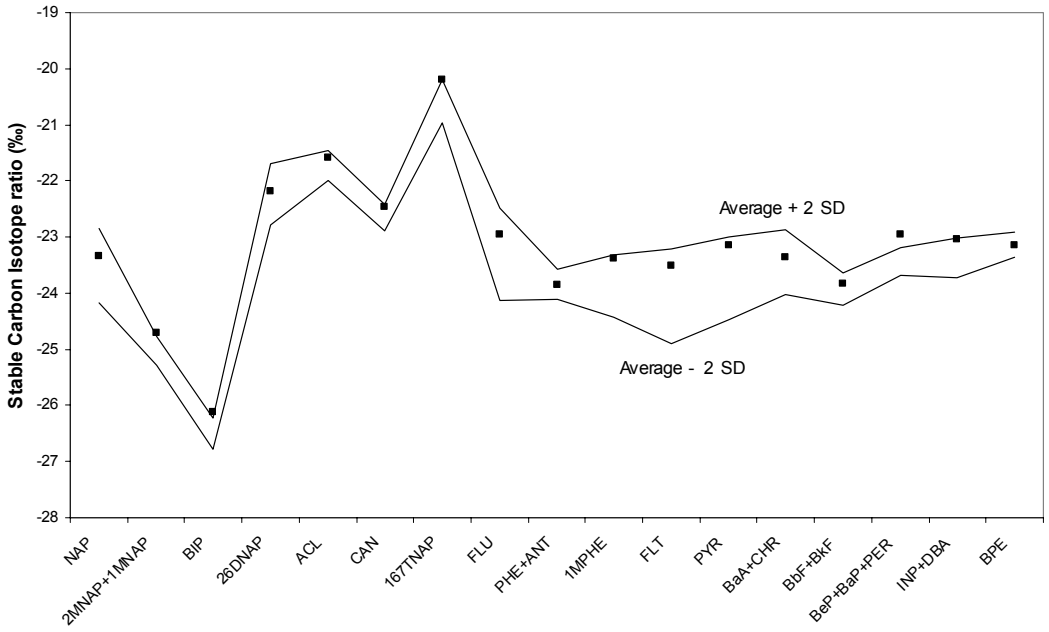


Fig. 4.22. Comparison of stable carbon isotope ratios between processed (■) and unprocessed (–) standard materials.

In this study, purification technique for compound specific stable carbon isotope ratio analysis was developed. The method includes alumina/silica gel column chromatography, gel permeation chromatography, and thin layer chromatography. The mean recovery of PAHs after the purification procedure was about 80 %. No isotopic fractionation was demonstrated during purification, although lower recoveries were seen for low molecular weight PAHs. Sample purities after purification were verified by GC/FID and full scan mass spectrometry.

GC/IRMS conditions were adjusted to better resolve peaks providing more accurate stable isotope analyses. For individual compounds or combined peaks, method precision ranged between 0.08 and 0.43 ‰. Precision increases with peak intensity because the contribution of background or interfering materials is greater for the smaller peaks. Method accuracy was confirmed using standard materials. The analytical protocols were evaluated to ensure compositional and stable isotopic integrity during purification. Most compounds exhibited isotopic conservation during purification. Some compounds exhibited some isotopic enrichment during purification, which may be caused by the preferential loss of isotopically light PAH during evaporation. The purification and analysis methods for the compound specific stable carbon isotope measurement provided good compound recovery, peak resolution and sensitivity, and precise and accurate isotopic ratios.

CHAPTER V

COMPOSITION AND STABLE CARBON ISOTOPE RATIO OF PAHS IN SEDIMENTS FROM THE LACUSTRINE ENVIRONMENT

PAHs are ubiquitous environmental contaminants. Many PAHs are stable and persistent in the environment and toxic. Extensive use of petroleum products and combustion of organic matter are the major sources of PAHs in the environment. Traditional method uses compositional information of PAHs to identify contaminant sources. However, chemical and biological alterations of pollutants often change the original composition of contaminants preventing a clear resolution of pollutant sources. Intrinsic tracers, such as stable carbon isotope ratios, are one approach that may better resolve sources of contaminants. Compound specific isotope analysis (CSIA) of contaminants has the potential to identify sources of pollutants in the environment.

The objectives of this study were to apply the developed purification and isotope analysis methods to lacustrine environmental samples and to test the applicability of the method. The study also includes the characterization of contaminant sources using PAH composition and isotope ratio data. To accurately measure the stable carbon isotope ratio of individual PAH compounds, sample extracts were purified using developed purification method involving various chromatographic and high performance liquid chromatographic techniques. The isolates were analyzed for PAH content and stable carbon isotope ratios. Stable carbon isotope ratios and quantitative compound distributions were used to trace and identify the source of the detected contaminants.

PAHs (including 16 EPA priority PAHs and alkylated homologues) in sediment were measured in urban lake sediments in the northwestern U.S. PAH distributions and stable carbon isotope ratios of PAHs were compared with those of sediment samples from reference sites including a shipping waterway, a harbor, and a relatively undisturbed remote lake. Total PAH concentrations in the urban lake sediments ranged from 66.0 to 16,500 μg/g dry wt with an average of 2,600 μg/g, which is on average about 50, 100,

and 400 times higher than harbor (48 μg/g on average), shipping waterway (26 μg/g), and the remote lake (7 μg/g) sediment samples, respectively (Fig. 5.1, Table 5.1).

The distribution patterns of individual PAHs at the four locations are shown in Fig. 5.2. Fluoranthene and pyrene were the most abundant PAH components in all areas except the remote lake, where perylene, which can have a biological origin, was the most abundant component. In all cases, high molecular weight PAHs (four- or more-ring PAHs) which are mainly produced by pyrogenic processes, were predominant over low molecular weight homologues (petrogenic origin). This result was expected in the highly populated and urbanized area of the study sites. In sediments from a shipping waterway, chrysene and benzo[b]fluoranthene showed relatively high concentrations, higher than in the other three sites. The PAH distribution patterns at the sites suggest a pyrogenic origin.

Sediment samples in the urban lake were collected during three different years, from July, 2000 through August, 2002. Temporal variation of PAH distributions was initially expected at the site but no regular trend in concentration over time was observed (Fig. 5.3). The variation between sampling appears to be due to the patchiness of PAH distributions throughout the lake sediments. Although temporal distribution patterns vary, it is clear that the PAH composition did not change over the 3 years of sampling period (Fig. 5.4). This also suggests that PAH sources in the study site were same over the three years and no preferential loss to biological degradation was apparent. If the PAHs at the site were heavily degraded, it would have been difficult to identify source of PAHs using compositional data alone. Changes in compositional distribution patterns result from the preferential loss of biologically and chemically labile compounds.

The methylphenanthrenes to phenanthrene ratio (MP / P) has been used to identify the source of hydrocarbon contaminants as pyrogenic or petrogenic. Pyrogenic sources produce PAH distributions dominated by the parent compounds of the 3-, 4-, and 5-ring PAHs, whereas petrogenic sources exhibit distribution patterns where alkylated PAHs far exceed the unsubstituted parent PAHs (Blumer, 1976). MP / P ratios in the study area (Fig. 5.5) showed that PAHs at the sites are primarily pyrogenic in origin. PAHs from the urban lake were pyrogenic whereas harbor sediment PAHs contained some

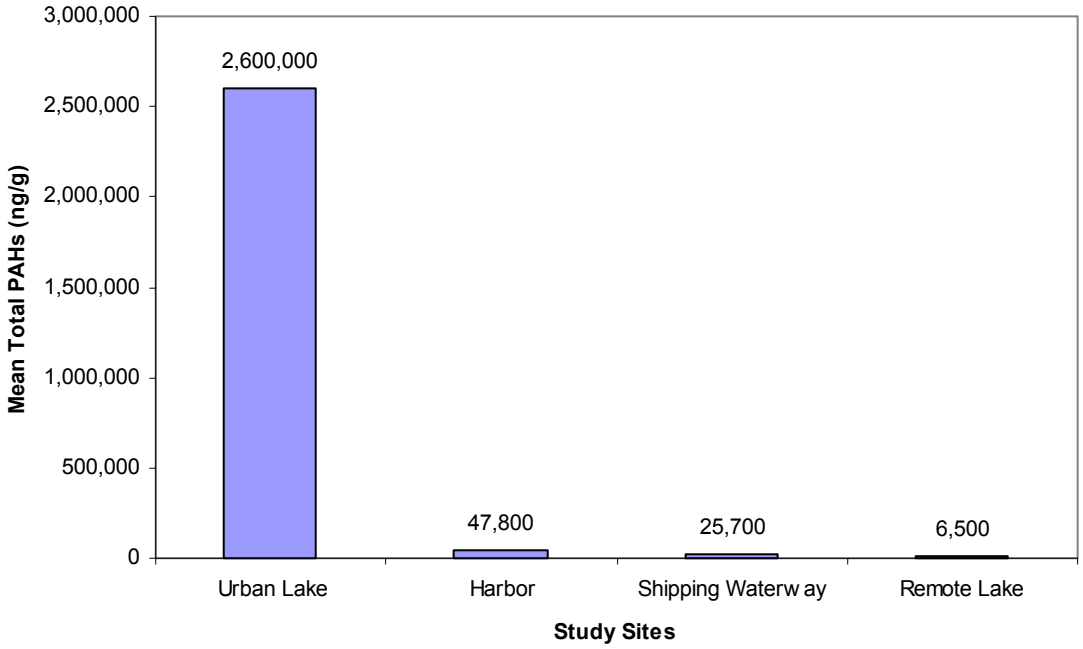


Fig. 5.1. Mean total PAH concentrations.

Table 5.1.
Mean PAH concentrations at the study sites.

Compounds	Urban Lake (n=50)	Harbor (n=3)	Shipping Waterway (n=3)	Remote Lake (n=6)
		(ng/g dry wt.)		
Naphthalene	38,272.2	633.7	137.4	83.0
C1-Naphthalenes	13,139.1	234.1	121.4	51.2
C2-Naphthalenes	12,627.6	179.6	140.5	56.6
C3-Naphthalenes	13,230.3	116.6	134.3	62.3
C4-Naphthalenes	6,660.8	75.8	107.0	42.4
Biphenyl	7,426.9	61.9	26.0	16.4
Acenaphthylene	13,965.3	239.6	75.6	27.6
Acenaphthene	51,266.2	223.8	190.8	71.8
Fluorene	29,274.3	392.4	275.7	81.4
C1-Fluorenes	10,146.4	259.1	110.0	51.5
C2-Fluorenes	8,950.6	436.3	276.2	70.8
C3-Fluorenes	6,760.1	577.9	225.8	72.2
Phenanthrene	200,731.4	965.1	825.6	422.3
Anthracene	103,057.9	2,397.8	787.3	198.3
C1-Phen/Anth	42,902.9	1,045.8	463.4	189.0
C2-Phen/Anth	20,885.8	886.3	350.1	130.7
C3-Phen/Anth	8,991.0	524.0	277.0	118.1
C4-Phen/Anth	3,535.3	259.5	177.3	183.0
Dibenzothiophene	31,971.4	79.6	68.2	26.5
C1-Dibenz	8,406.8	64.2	50.4	20.9
C2-Dibenz	5,374.0	125.3	81.4	28.9
C3-Dibenz	3,079.4	186.8	327.5	54.5
Fluoranthene	321,163.1	5,764.4	2,777.5	620.2
Pyrene	378,433.0	7,436.6	2,866.3	605.1
C1-Fluor/Pyr	68,681.3	5,048.4	1,783.7	455.0
Benz(a)anthracene	116,468.8	3,030.9	1,299.4	221.4
Chrysene	119,188.7	3,616.7	2,592.8	273.1
C1-Chyrsenes	23,241.1	1,578.8	671.1	122.4
C2-Chrysenes	6,383.9	446.0	256.0	76.9
C3-Chrysenes	353.9	19.2	29.3	16.9
C4-Chrysenes	3,262.0	78.9	63.4	7.3
Benzo(b)fluoranthene	157,294.1	3,436.0	2,592.5	341.1
Benzo(k)fluoranthene	47,471.4	1,091.1	781.2	87.2
Benzo(e)pyrene	104,849.5	1,479.1	1,354.7	194.2
Benzo(a)pyrene	249,042.1	2,730.1	1,550.9	347.4
Perylene	45,260.7	530.4	327.3	698.0
Indeno[1,2,3-cd]pyrene	152,695.9	732.6	707.3	222.0
Dibenz(a,h)anthracene	11,897.0	201.1	170.6	29.0
Benzo(ghi)perylene	152,582.4	579.2	697.3	217.2
Total PAHs	**2,598,925.0**	**47,764.8**	**25,658.2**	**6,543.5**
Specific Isomers				
2-Methylnaphthalene	7,106.4	128.1	77.0	29.3
1-Methylnaphthalene	6,032.7	105.9	44.4	21.9
2,6-Dimethylnaphthalene	6,083.4	125.6	92.3	22.9
1,6,7-Trimethylnaphthalene	3,669.1	35.5	49.6	20.1
1-Methylphenanthrene	11,187.6	318.2	136.3	59.3

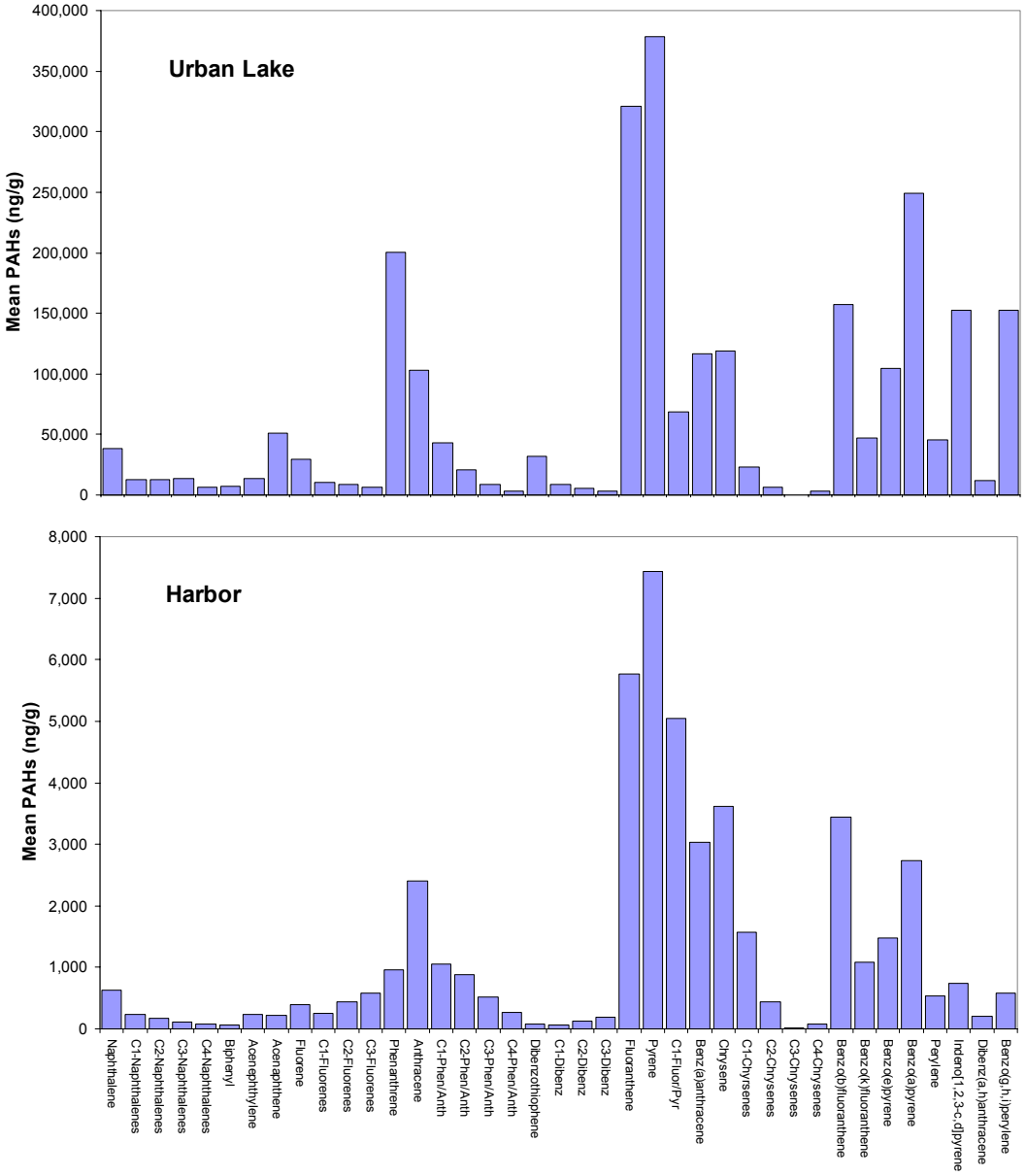


Fig. 5.2. PAH distribution patterns at the study sites.

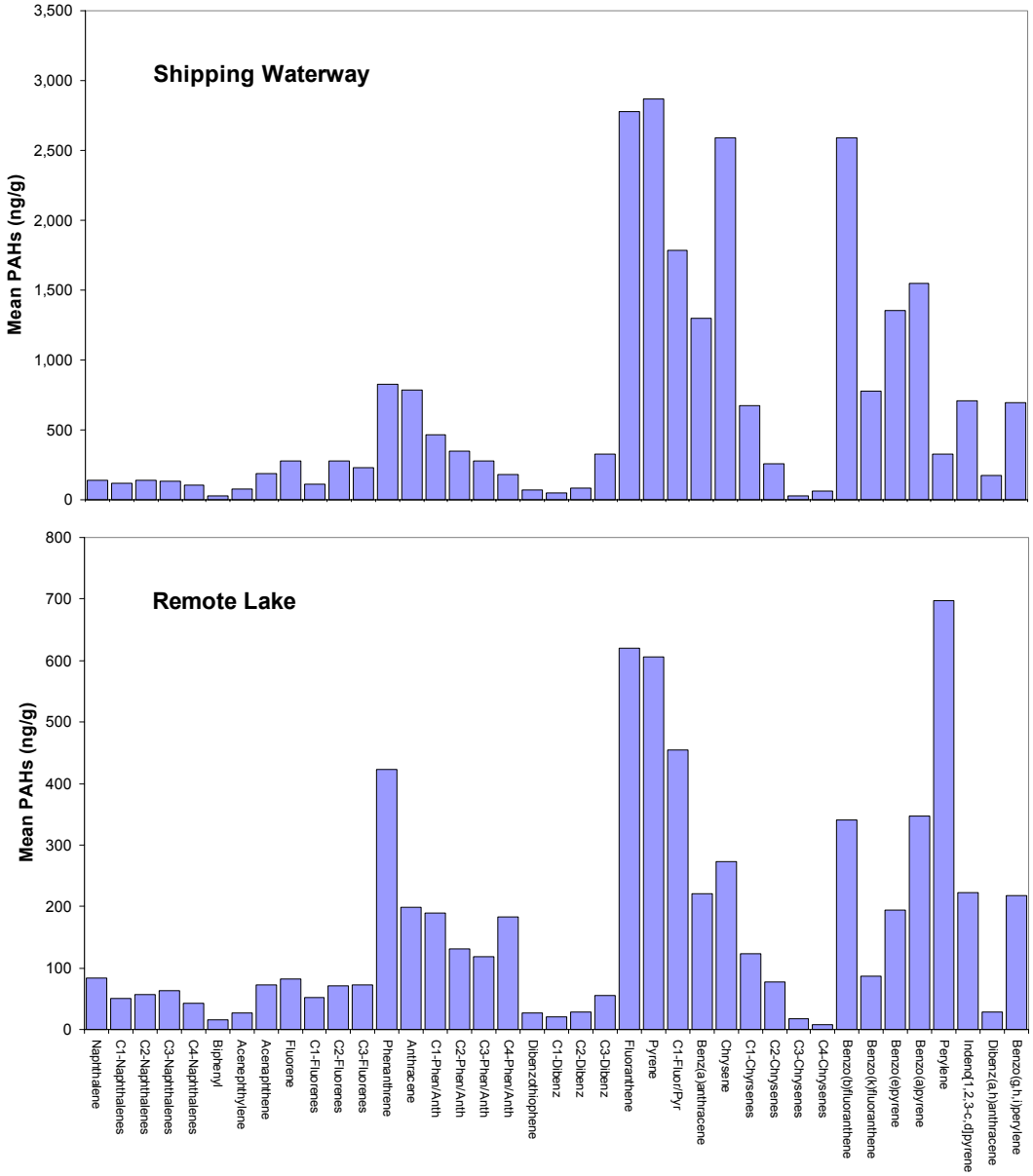


Fig. 5.2. Continued.

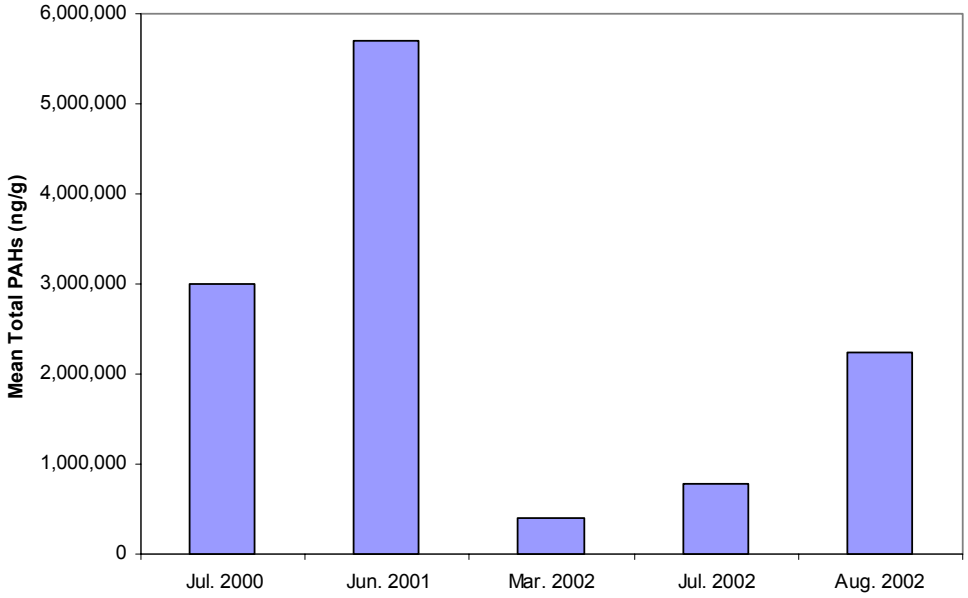


Fig. 5.3. Temporal variation of mean total PAH concentrations in the urban lake sediments.

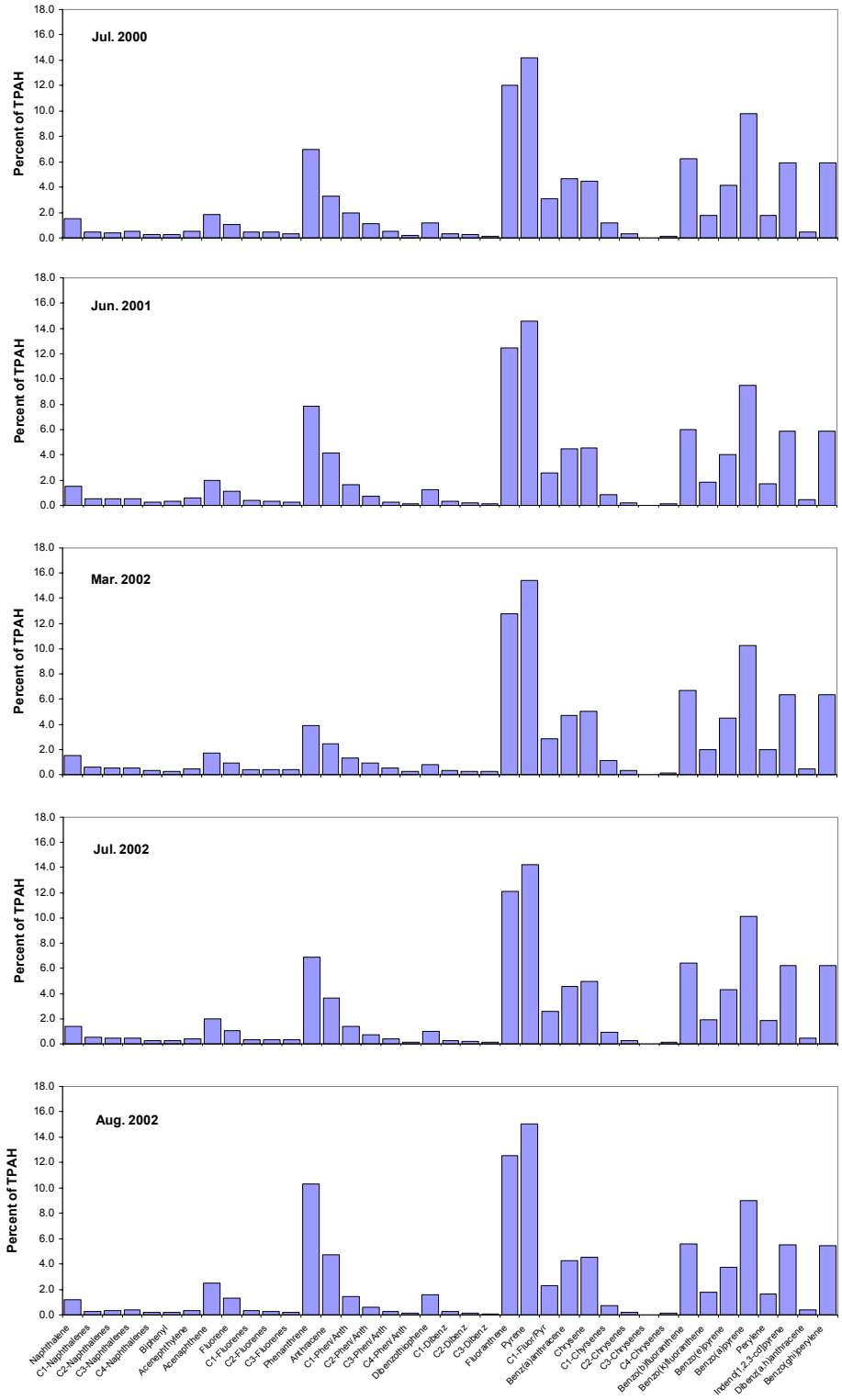


Fig. 5.4. Relative percent distribution patterns of PAHs in the study sites.

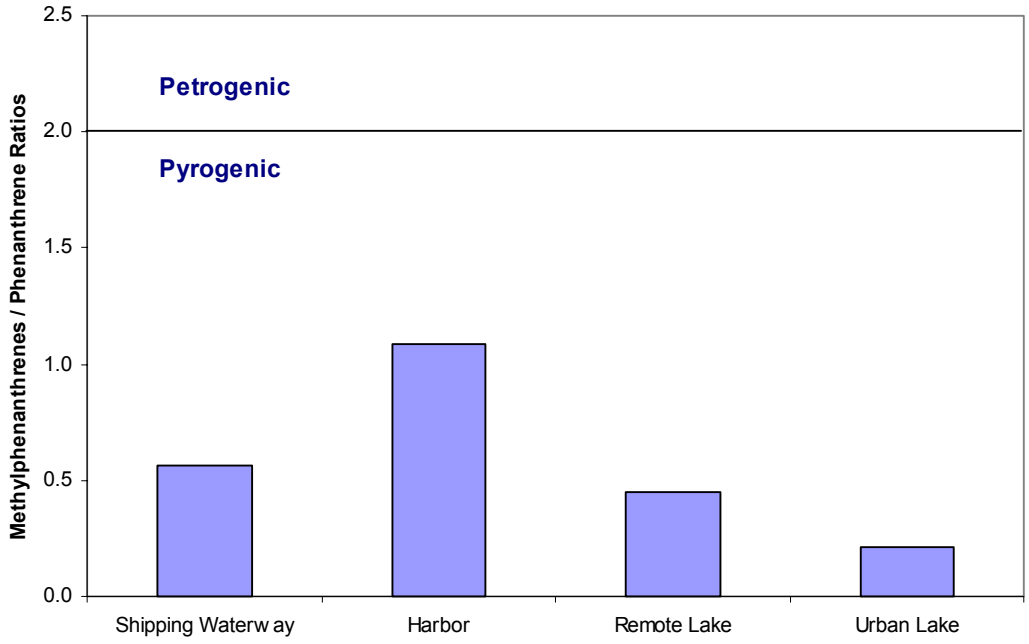


Fig. 5.5. Ratios of methylphenanthrenes to phenanthrene (MP / P).

petrogenic hydrocarbons although they exhibit pyrogenic inputs (MP / P less than 2). The pyrogenic origin of the urban lake PAHs was also confirmed by using the pyrogenic index (Fig. 5.6). The pyrogenic index is the ratio of the sum of the concentrations of the other EPA priority unsubstituted three- to six-ring PAHs to the sum of the concentrations of five targeted alkylated PAH homologues (naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes, chrysenes). Other EPA priority unsubstituted PAHs include biphenyl, acenaphthylene, acenaphthene, anthracene, fluoranthene, pyrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene. Values have been reported to be in a range of 0.8 – 2.0 for soot samples (Wang et al., 1999). All four study areas exhibited primarily pyrogenic inputs with the PAHs in the urban lake sediments the most pyrogenic in nature.

Several PAH molecular ratios have been used to differentiate sources of PAH in contaminated samples. C2-dibenzothiophenes / C2-phenanthrenes (C2-Db / C2-Ph) and C3-dibenzothiophenes / C3-phenanthrene (C3-Db / C3-Ph) PAH ratios, which vary among oils having different sulfur contents, were shown to be relatively constant and may be useful in identifying oil sources even after heavy degradation (Page et al., 1995; Bence et al., 1996). In this study, the C2-Db / C2-Ph ratios (Fig. 5.7) and the C3-Db / C3-Ph ratios (Fig. 5.8) were relatively unchanged and could be used to differentiate sources. Urban lake, remote lake, and harbor samples are clearly different based on the C3-Db / C3-Ph ratios and may indicate that these three sites have different sources of PAH contamination.

Bence et al. (1996) reported that C2-chrysenes / C2-phenanthrenes (C2-Ch / C2-Ph) ratio were sensitive to weathering because of the higher solubility of phenanthrenes in water than chrysenes, whereas C2-Db / C2-Ph ratio remains relatively unchanged. In this study, however, C2-Ch / C2-Ph ratios were relatively constant at each study site and could be used to differentiate harbor and shipping waterway PAHs from the urban lake sediment PAHs (Fig. 5.9). Sediments from the harbor (1.6) and shipping waterway (1.5)

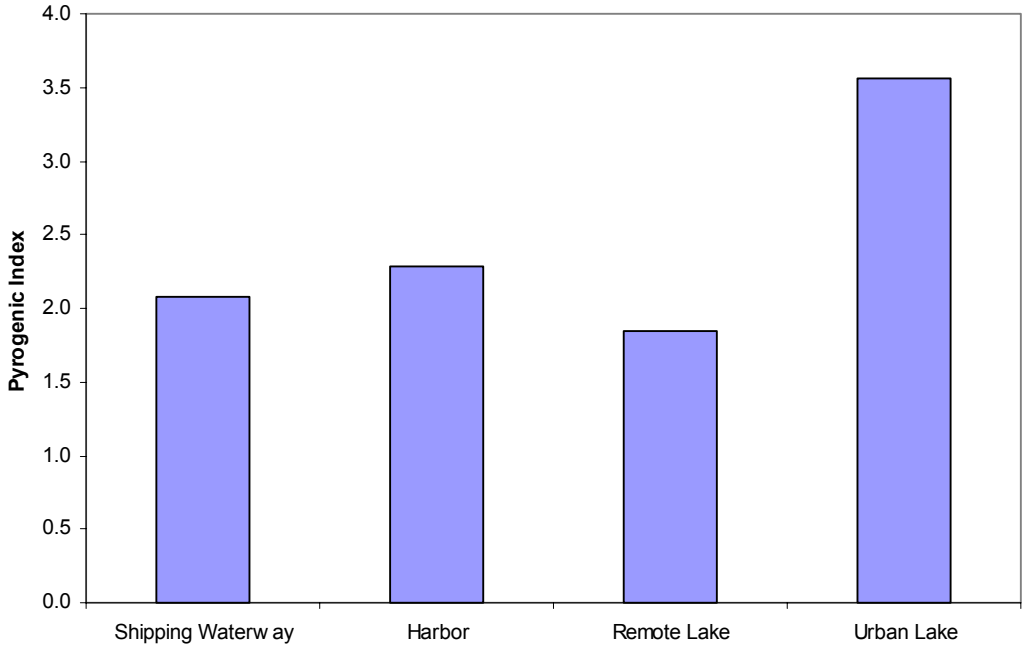


Fig. 5.6. Pyrogenic indices at the study sites.

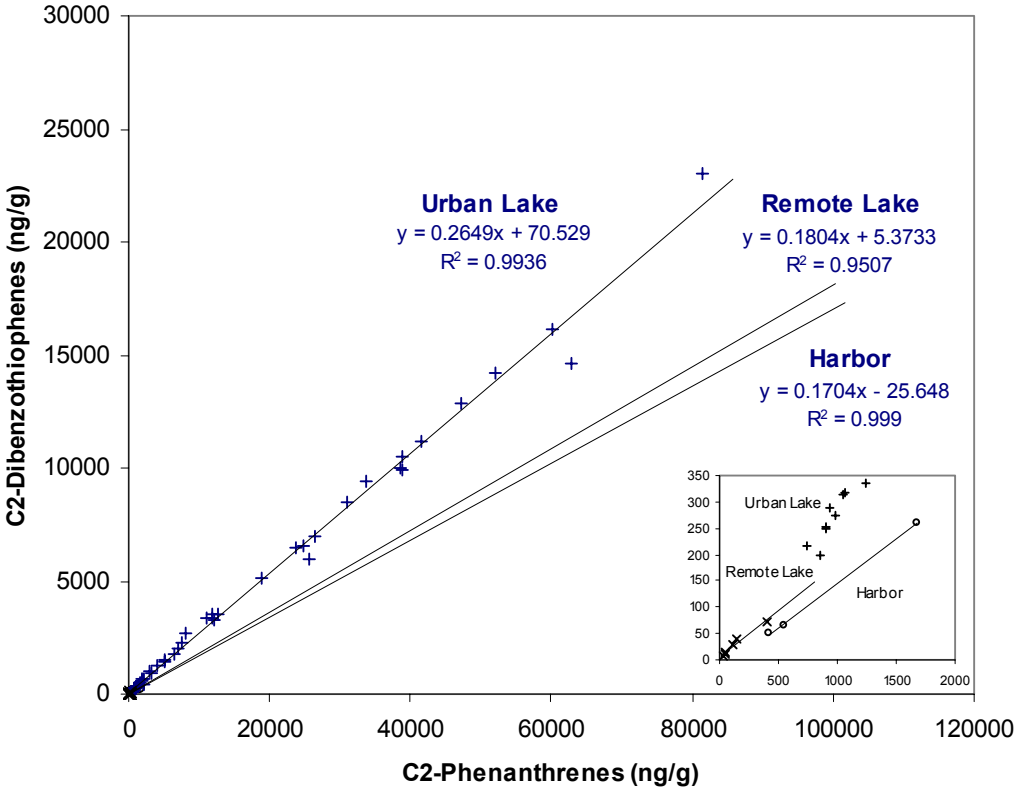


Fig. 5.7. Plot of C2-phenanthrenes vs. C2-dibenzothiophenes.

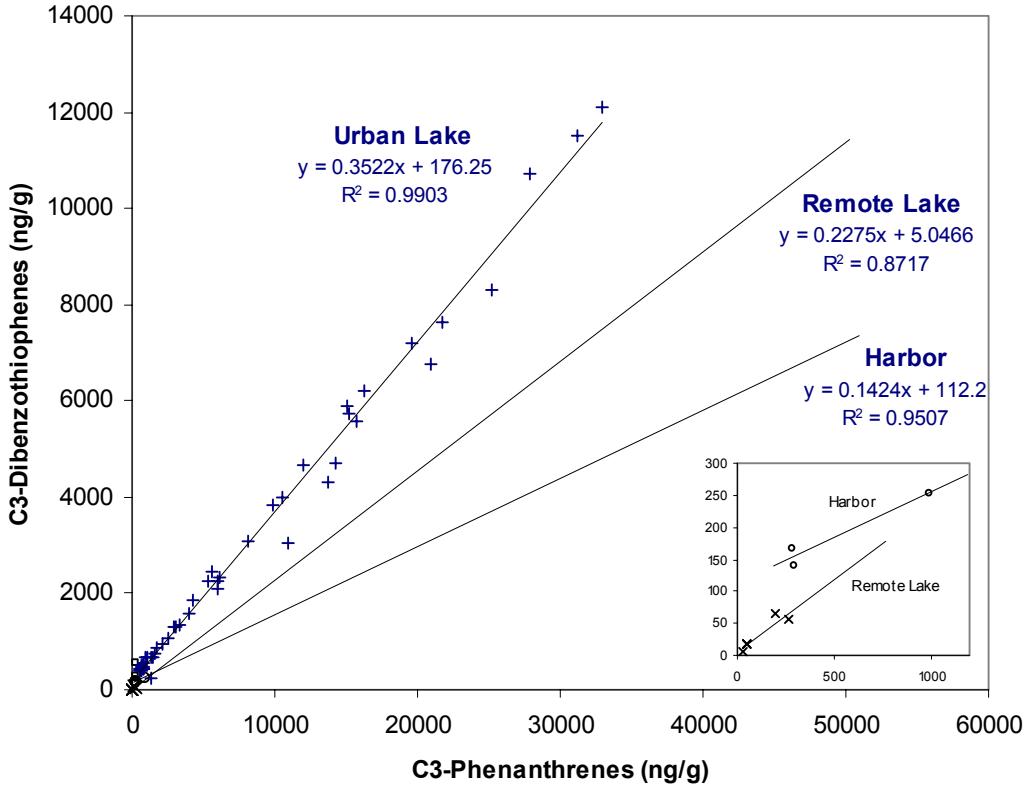


Fig. 5.8. Plot of C3-phenanthrenes vs. C3-dibenzothiophenes.

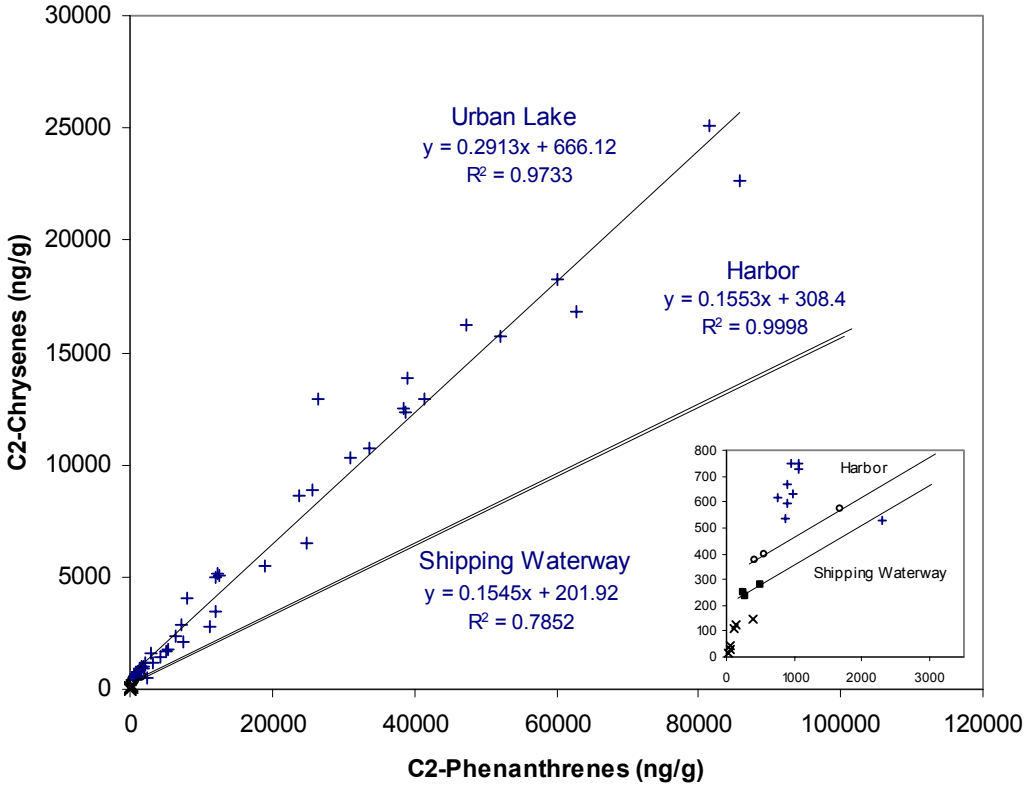


Fig. 5.9. Plot of C2-phenanthrenes vs. C2-chrysenes.

exhibited similar ratios implying similar sources of PAH or similar degrees of degradation at both sites.

When two molecular ratios were compared, the urban lake samples showed a more pyrogenic tendency than the other sites (Fig. 5.10 and Fig. 5.11). This indicates that the urban lake PAH has a distinctive source of PAHs different from the other study sites. Using the pyrogenic index and phenanthrene / anthracene ratios (Fig. 5.12), the four study sites can be differentiated. It also indicates that samples from the urban lake have a unique source of contamination that is different from the contamination at the nearby reference sites in the same watershed, e.g., shipping waterway, harbor and remote lake sediments.

The PAH data were analyzed using Principal Component Analysis (PCA). All measured parent and alkylated PAH data were included in the analysis. SPSS 11.5 for Windows (SPSS Inc., Chicago, Illinois) were used to perform PCA. To make each variable have the same influence in the PCA, the entire data matrix was standardized by subtracting the mean and dividing by the standard deviation. This standardization makes the centroid of the whole data set zero and assigns every variable a variance of 1.0. Loading plots of two principal components of the total three extracted components are illustrated in Fig. 5.13. In the loading plot of compounds, unalkylated parent PAHs showing high loading can be separated from alkylated PAHs in PC 1. PC 3 may separate compounds according to their molecular weight. High molecular weight PAHs seem to be highly related with PC 3. Pyrogenic PAHs, including fluoranthene, pyrene, benzofluoranthene and benzoperylene, are highly loaded in both PC 1 and PC 3 and show close similarity each other suggesting same origin for those pyrogenic PAHs in the study area. Other petrogenic or alkylated PAHs may be explained by various petrogenic sources. Study areas can be clearly differentiated in the loading plot of PC 1 and PC 2 of PAHs data. The urban lake sediments which showed high loading in both PC 1 and PC 2 can be explained by their unique source of contamination different from the contamination at the other sites.

Compound specific isotope analysis suggested a mixture of sources for PAHs in the

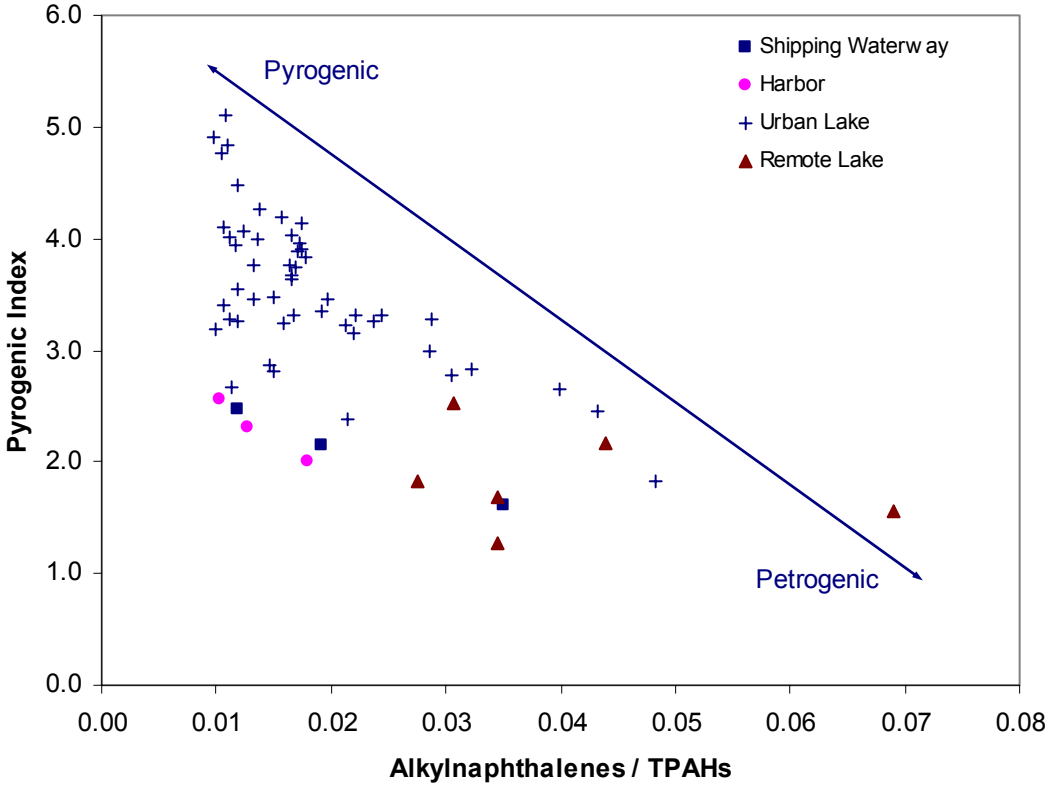


Fig. 5.10. Plot of pyrogenic index against alkylnaphthalenes to total PAH ratios.

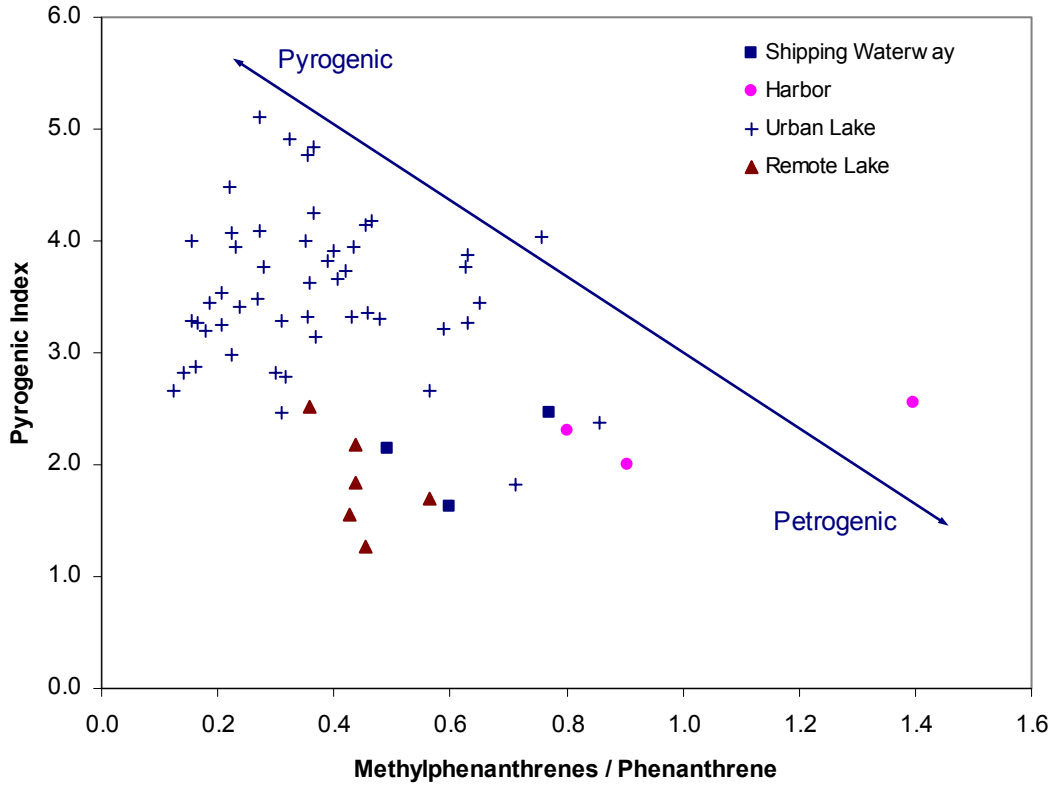


Fig. 5.11. Plot of pyrogenic index against methylphenanthrenes to phenanthrene ratios.

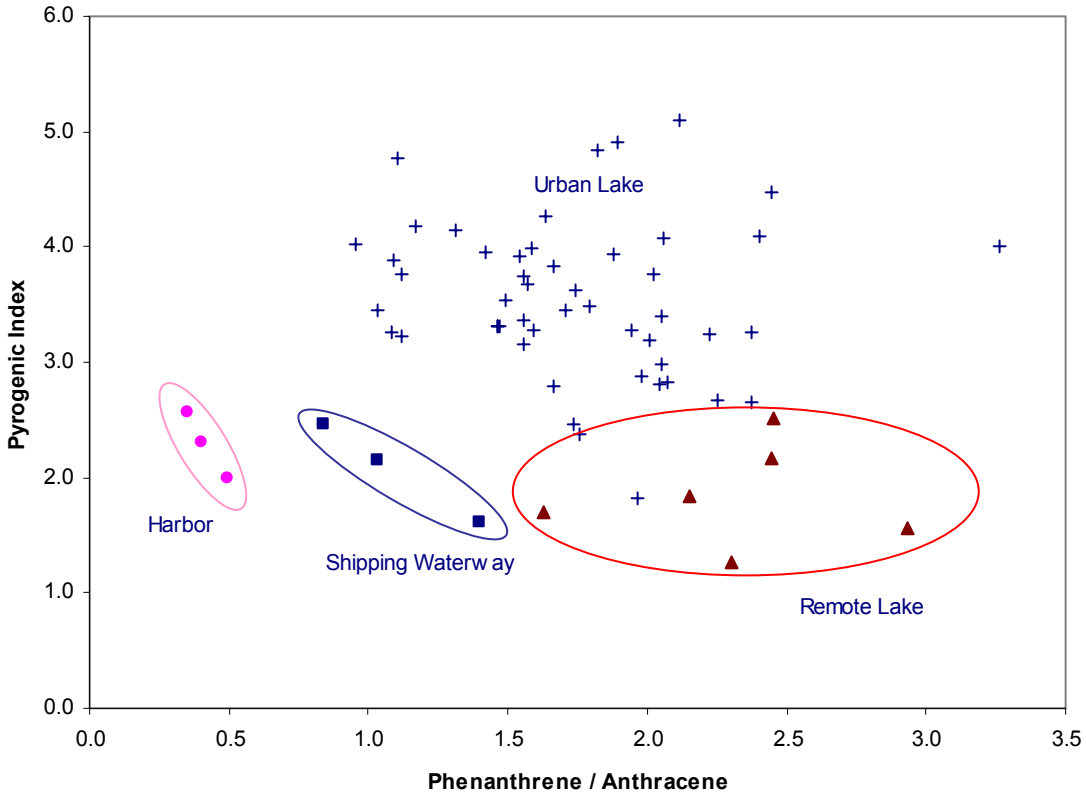


Fig. 5.12. Plot of pyrogenic index against phenanthrene to anthracene ratios.

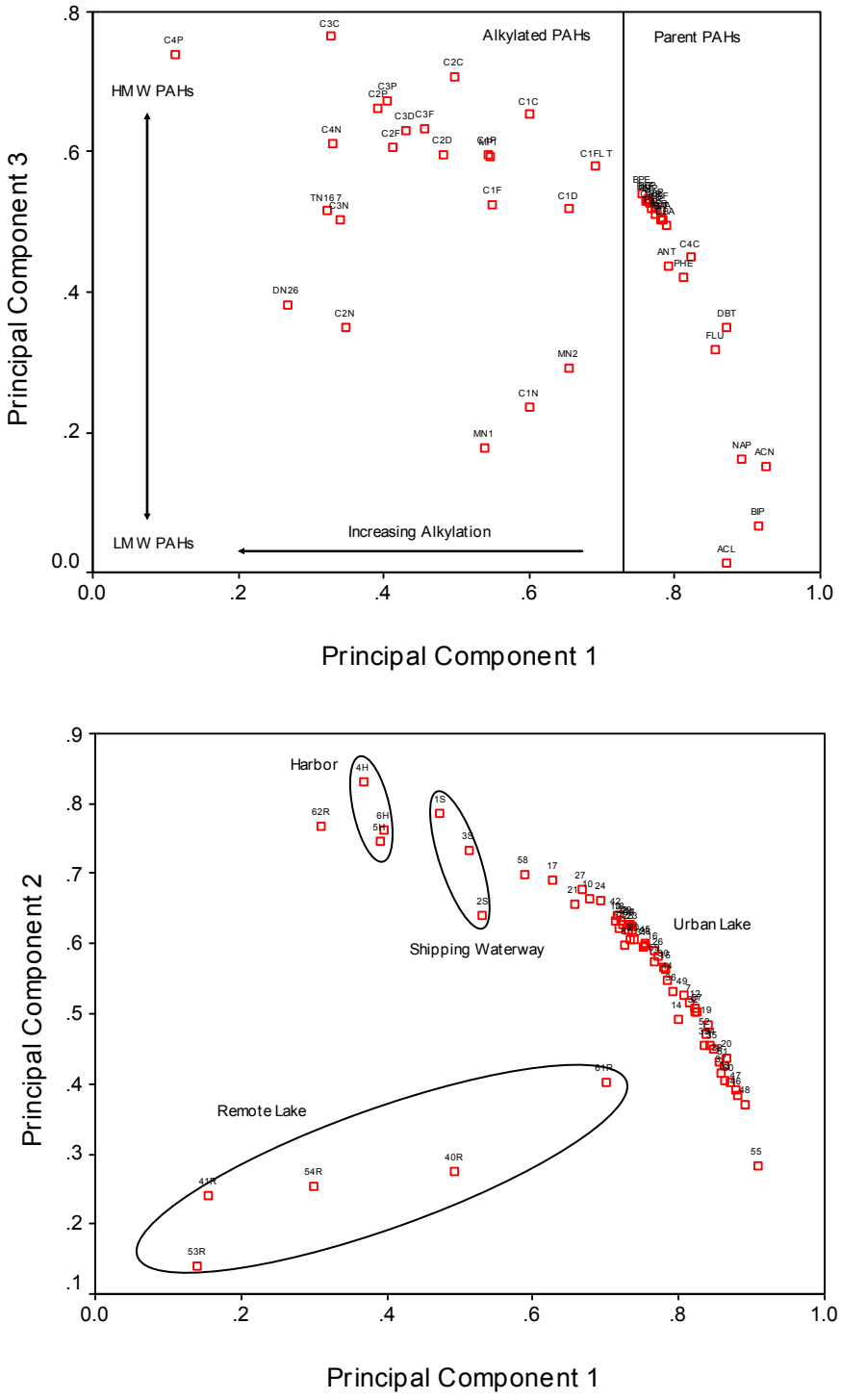


Fig. 5.13. Plots of principal components for the Principal Component Analysis of sediment PAH data from the study sites.

study area. The stable carbon isotope ratios of PAHs from the study sites are shown in Fig. 5.14. The error bar shows ± 1 standard deviation for all measured urban lake samples. For low molecular weight PAHs, samples from the urban lake exhibited enrichment in ^{13}C compounds, which is the characteristics of a pyrogenic origin, suggesting distinctive sources from the other sites. For high molecular weight PAHs, PAHs in the remote lake sediment showed depletion in ^{13}C compounds, which is the characteristics of a petrogenic origin, while the urban lake, shipping waterway and harbor samples showed similar isotope ratios to each other implying similar sources for the contaminants in these areas. The remote lake is located upstream of the urban lake, possibly minimizing the effect from the urban lake, while the shipping waterway and harbor samples were collected downstream of the urban lake. Shipping waterway and harbor sediments which have petrogenic origin for the low molecular weight PAHs may have great influences from the urban lake for high molecular weight PAHs produced uniquely at the site. This compound specific isotope analysis of PAHs confirmed the uniqueness of the source of the urban lake PAHs.

Stable carbon isotope ratios of the urban lake sediments show large variability for low molecular weight PAHs while high molecular weight PAHs show very stable and constant stable isotope ratios (Fig. 5.14 and 5.15). This high variability for the low molecular weight PAHs may be the reflections of variety of sources for the compounds and the differing degrees of degradation once they are deposited. For high molecular weight PAHs, single source or simple mixtures of sources are anticipated and they are subjected to little degradation. There was somewhat of a depletion in stable carbon isotope ratios with increasing molecular weight, especially high molecular weight compounds (Fig. 5.14 and 5.16). Chemical reactions always show a preferential enrichment of the lighter isotope in the reaction products because molecules bearing the light isotope will react slightly more readily than those with the heavy isotope (Hoefs, 1997). Production of higher molecular weight PAHs involves more recombination reactions than low molecular weight compounds during pyrosynthesis which tends toward enrichment in the lighter isotope.

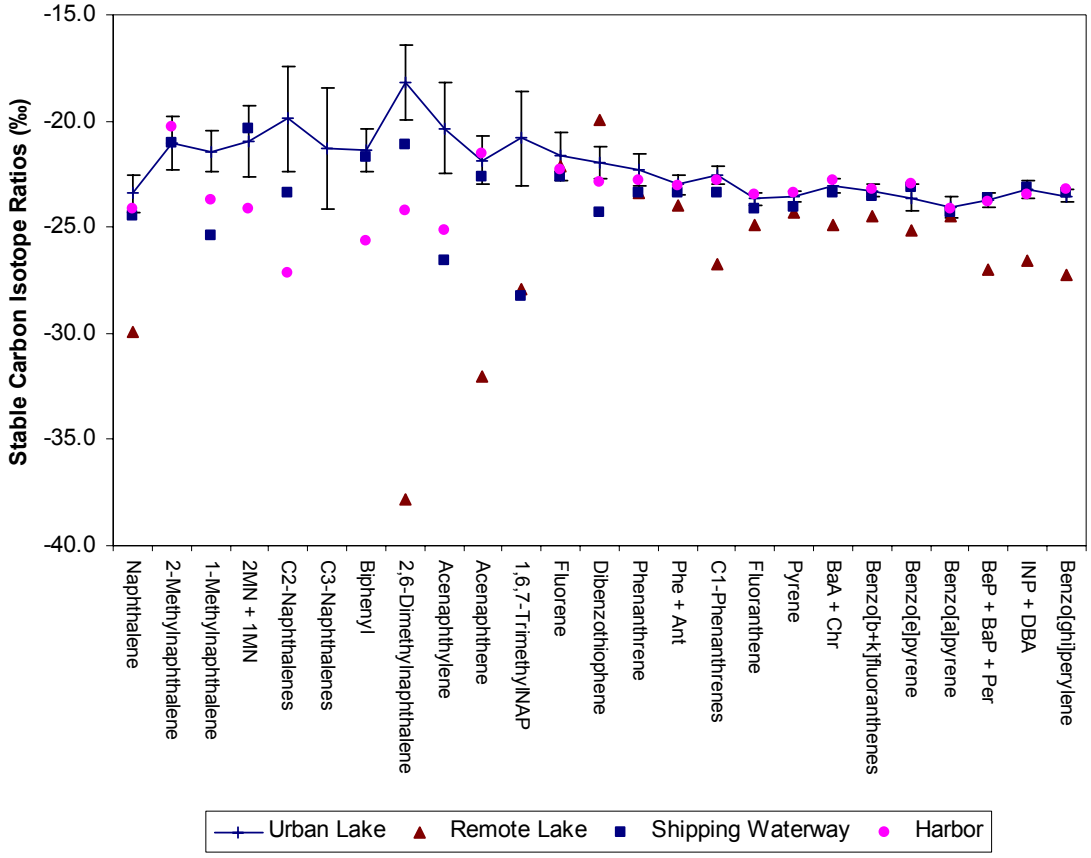


Fig. 5.14. Stable carbon isotope ratios of PAHs at the study sites.

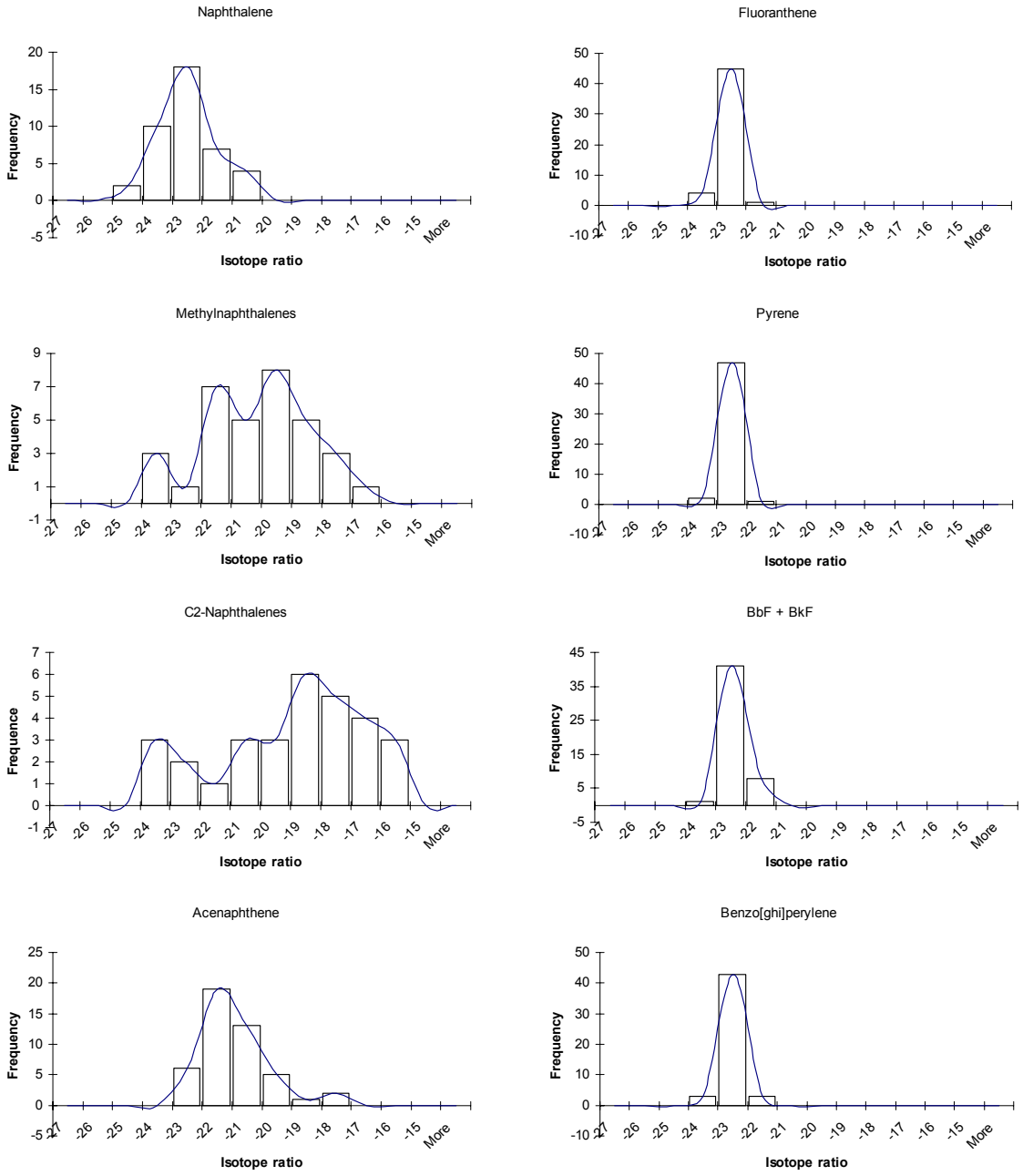


Fig. 5.15. Frequency histograms of stable carbon isotope ratio of PAHs in the urban lake sediment samples.

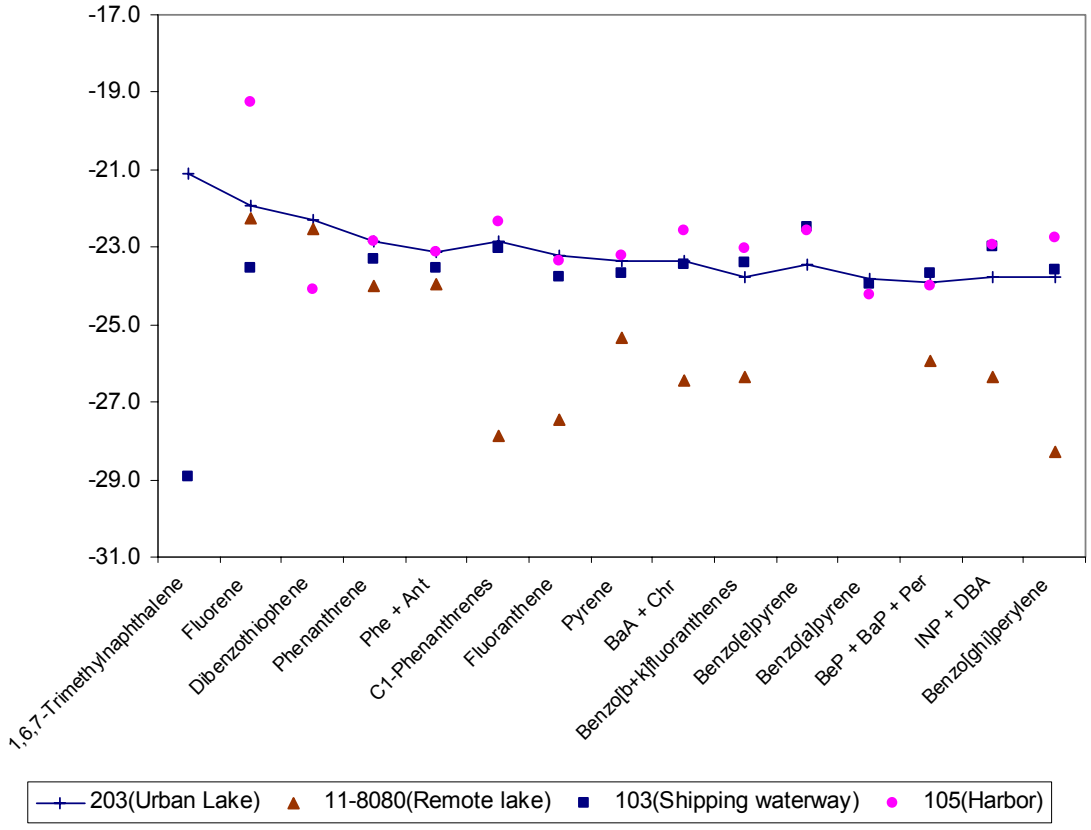


Fig. 5.16. Stable carbon isotope ratios of high molecular weight PAHs from selected samples at the study sites.

Stable carbon isotope ratios of PAH in urban lake sediments were analyzed for temporal variations during the study period. Unlike high molecular weight PAHs, which showed relatively constant stable carbon isotope ratios during the study period, naphthalene and methylnaphthalenes showed gradual enrichment of heavy isotope compounds during the study period (Fig. 5.17). This enrichment seems to be due to the biodegradation or physicochemical processes which involve kinetic isotopic fractionation or isotope exchange effect. During the biodegradation processes, isotopically light compounds are preferentially attacked and degraded by microorganisms. Physicochemical processes like evaporation or condensation processes, also involve isotopic fractionation by isotope exchange effect which results in preferential enrichment of lighter molecular species in the vapor phase and enrichment of heavier molecules in sediments (Hoefs, 1997). Although relatively variable in the stable isotope ratios, no temporal variations or fractionations were observed for low molecular weight PAHs other than naphthalenes. Variations in isotope ratios for these compounds are mainly explained by variation in sources or by the differing degrees of contributions to the mixture.

The relationship between stable carbon isotope ratios and concentration of selected PAHs is shown in Fig. 5.18. For petrogenic PAHs, like acenaphthene and C1-phenanthrenes, stable carbon isotope ratios are lighter as the concentrations of the compounds decrease, at lower concentration range (especially for the remote lake samples), whereas stable carbon isotope ratios for pyrogenic PAHs are relatively constant. This suggests a single source or a relatively simple mixture of sources for pyrene and benzo[b+k]fluoranthenes, but multiple sources for acenaphthene and C1-phenanthrenes. Mixed sources of petrogenic PAHs are also recognizable in low concentration samples, e.g., the remote lake, shipping waterway, and harbor sediments.

The relationship of stable carbon isotope ratios in two specific PAH compounds are illustrated in Fig. 5.19. Although four study sites are not clearly separated on the figures, remote lake PAHs are clearly different from the other sites' PAHs. Petrogenic contributions to the remote lake PAHs are recognizable. Stable carbon isotope ratios of

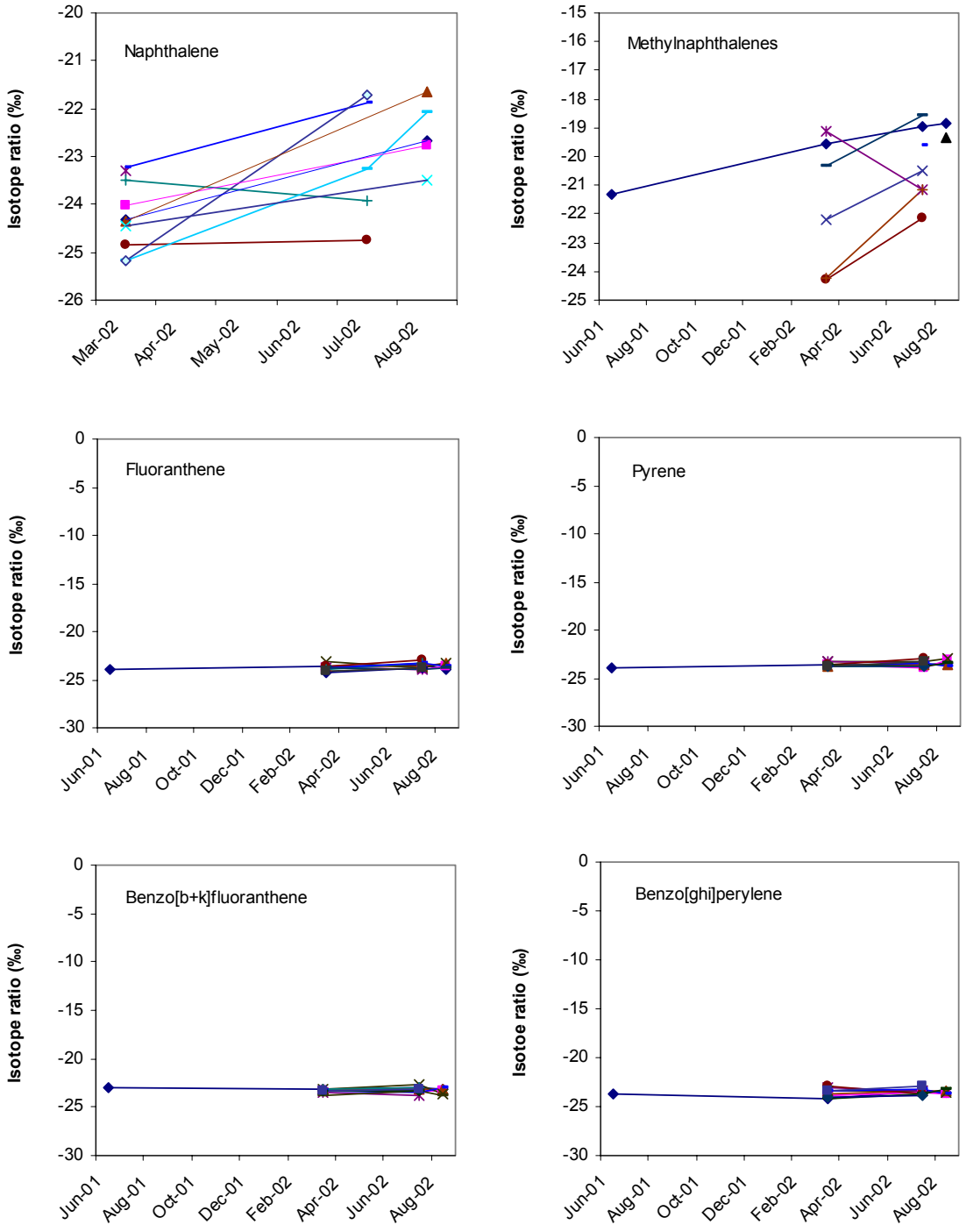


Fig. 5.17. Temporal variations of stable carbon isotope ratios of selected PAHs during the study period of 2001 – 2002.

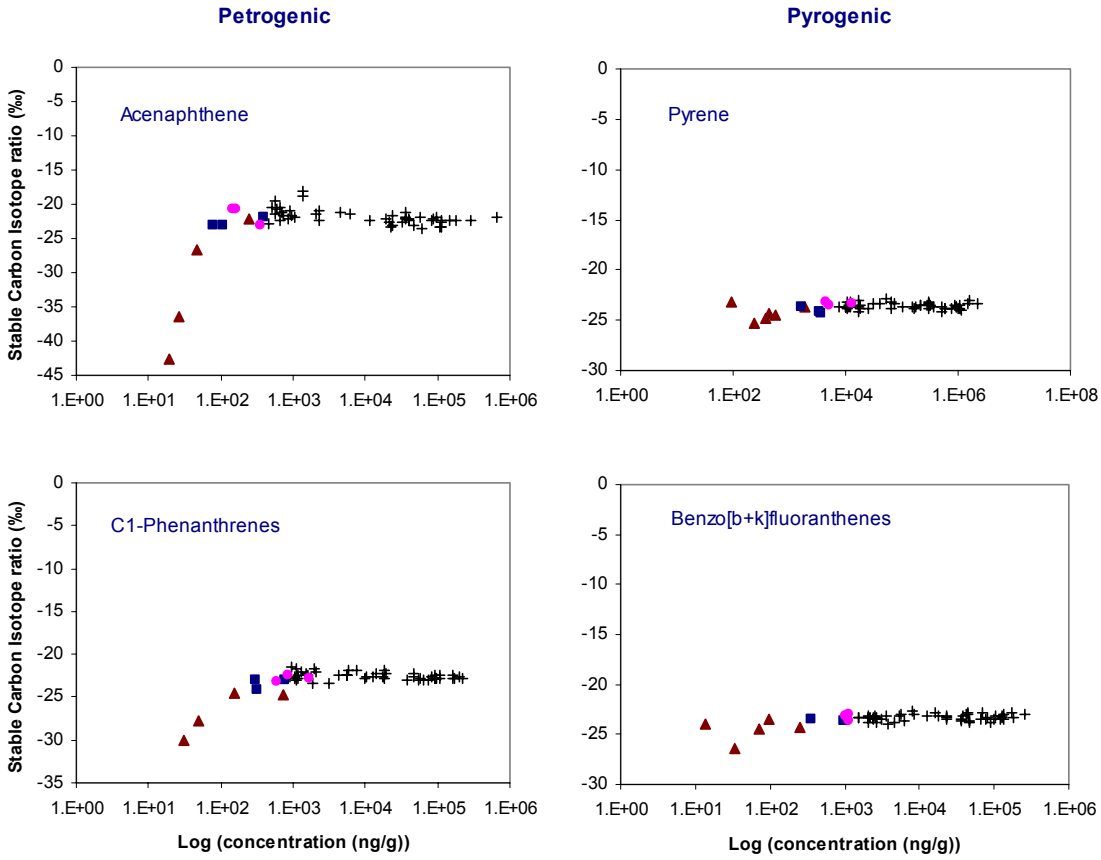


Fig. 5.18. Relationship between stable carbon isotope ratios and concentrations of selected PAHs.

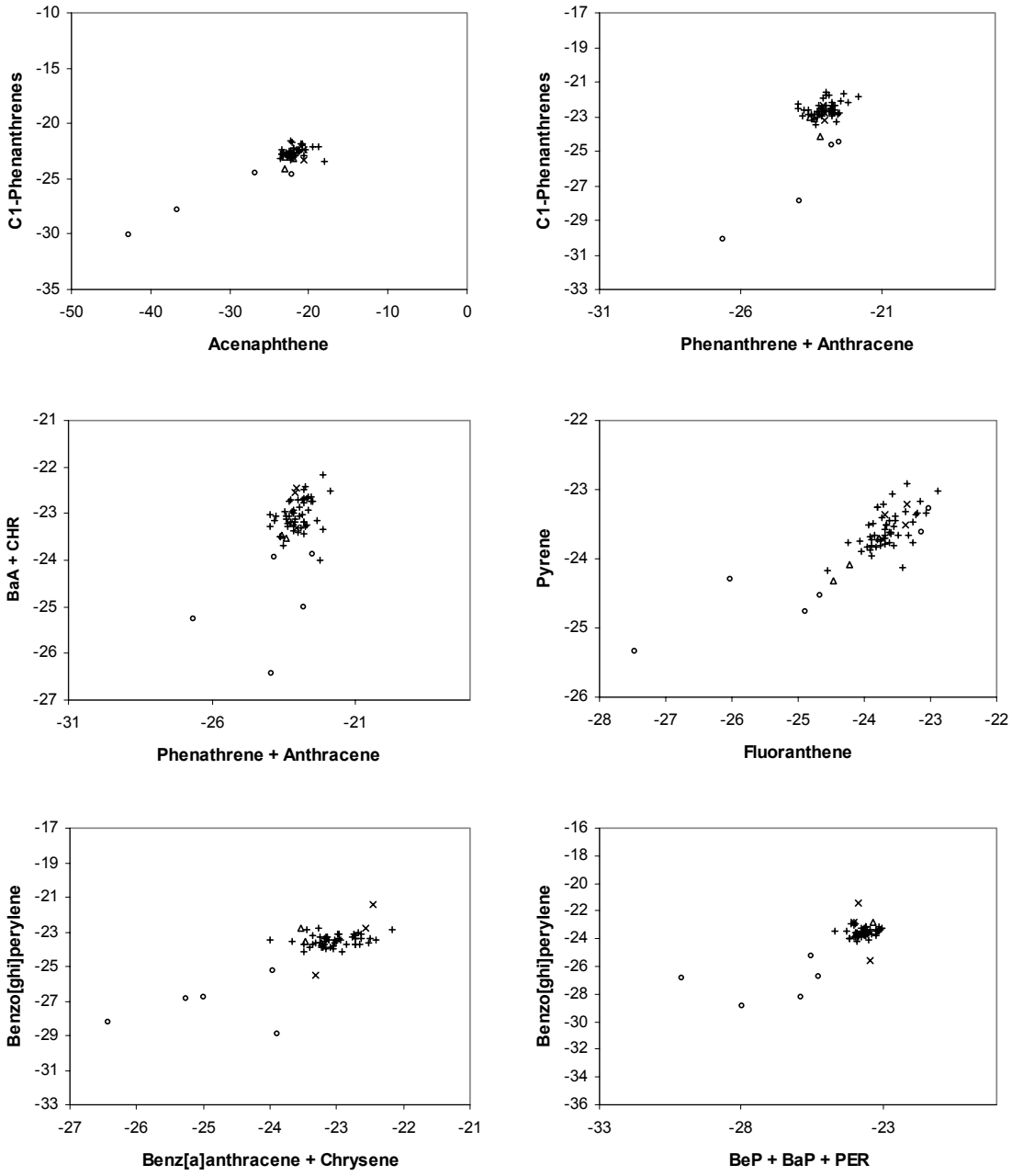


Fig. 5.19. Plots showing relationship of stable carbon isotope ratios between two selected PAHs.

petroleum show depletion in heavy isotope due to the preferential loss of labile compounds, such as carbohydrates which are enriched in ^{13}C, during the early diagenesis and maturation processes.

Due to the lack of the stable isotope values of end members, direct comparison of stable isotope ratios with possible sources or quantitative source apportionment using mass balance equation were impossible in this study. Instead, stable carbon isotope ratios of some PAHs were compared with those from the published data (O'Malley et al., 1996) in Fig. 5.20. Crankcase oil which can be one of the major petrogenic source in an urbanized area has stable carbon isotope ratios between – 27 ~ – 29 ‰ for fluoranthene, pyrene, benzofluoranthene, benz[a]anthracene, and chrysene. Car soots and wood fire soots, which are major sources of pyrogenic PAHs, have stable carbon isotope ratios around – 25 ‰. However the urban lake PAHs have higher enrichment in ^{13}C compounds than car soots and fire soots implying a distinctive source. Petrogenic contributions are clearly observed for fluoranthene and benz[a]anthracene + chrysene in some samples while pyrene and benzofluoranthene do not show clear evidence for a contribution from crankcase oil. While PAHs in the urban lake sediments, which showing pyrogenic characteristics, seemed to be produced by very unique processes which is different from car soot or fire soot production, PAHs from the other sites in the same watershed with the urban lake, were supposed to be the result of mixing of the urban lake PAHs with the contributions from other possible sources including pyrogenic emission from industrial and domestic processes and petrogenic emission from land and water transportation systems.

PAHs in the urban lake sediments are characterized by the high concentrations, up to a percent level, their pyrogenic properties, and the distinctive molecular and isotopic signatures. The uniqueness of the source of the sediment PAHs is illustrated by PAH molecular ratios and confirmed by stable carbon isotope ratios. The unique pyrogenic properties most likely originate from the coal gasification processes that occurred in the area for more than 50 years. The constancy of molecular ratios and stable carbon isotope ratios over the sampling period of 3 years confirmed that the source in the study sites

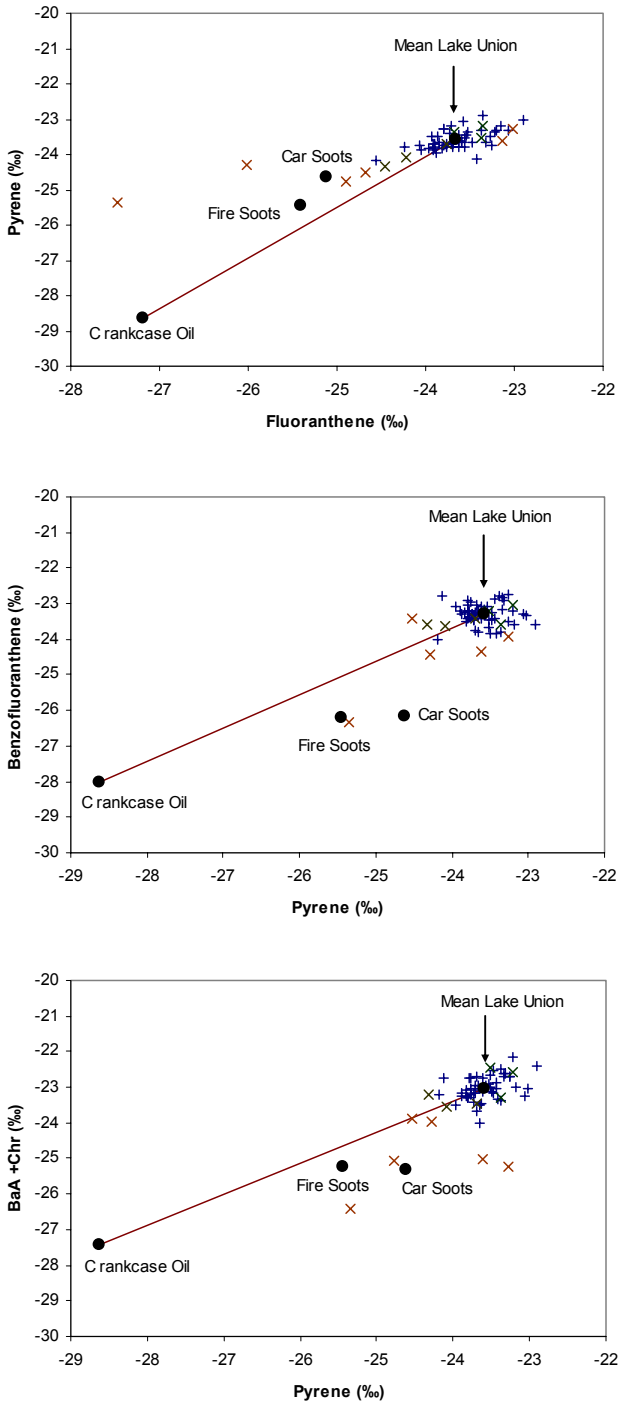


Fig. 5.20. Stable carbon isotope ratios of selected PAHs in the study sites and comparison with the value of crankcase oil, fire soots and car soots (Values for crankcase oil, fire soots and car soots are from O'Malley *et al*. (1996)).

were the same and probably occurred sometime in the past. This study confirms that developed methods for purification and compound specific isotope analysis of pollutant extracts by gas chromatography linked with an isotope ratio mass spectrometer can be used to identify PAH origins in natural systems. Quantitative source apportionment may be possible using a mass balance approach if end members are well-defined. GC/IRMS measurement of stable isotopic compositions for the purpose of tracing contaminants can be an effective additional method used in conjunction with traditional molecular methods.

CHAPTER VI

COMPOSITION AND STABLE CARBON ISOTOPE RATIO OF PAHS IN SOILS AND SEDIMENTS FROM THE MCMURDO STATION, ANTARCTICA

While Antarctica is often seen as pristine, humans have been impacting the environment for many decades (Kennicutt *et al*., 1992; Kennicutt *et al*., 1995; Aislabie *et al*., 1999; Aislabie *et al*., 2000). For example, atmospheric transport from the lower latitudes brings pollutants into Antarctica (Patton *et al*., 1991). Human activities on the continent produce pollutants that can be observed near locations of human habitation. The main human activities in Antarctica include scientific research, research support activities, vessel and vehicle traffic, waste disposal, tourism and fishing (Cripps and Priddle, 1991; Aislabie *et al*., 1999). All of these activities require fuel storage, consumption and fueling. Accidental fuel spills on land mainly occur near scientific stations where storage and refueling of aircraft and vehicles take place (Cripps and Priddle, 1991). Sub-tidal sediment contamination can originate from oil spills, ship operations and run-off from adjacent land areas (Kennicutt *et al*., 1992; McDonald *et al*., 1992).

The most widespread contaminants in Antarctica result from the use of petroleum products (Cripps and Priddle, 1991; Kennicutt *et al*., 1992; McDonald *et al*., 1992). Petroleum products contain many compounds, including PAHs that have been shown to have toxicological effects in organisms. PAHs are ubiquitous environmental contaminants. The hydrophobicity and low volatility of high molecular weight PAHs lead to their persistence in the environment.

The objectives of this study were to use purification and isotope analysis methods to analyze samples from McMurdo Station, Antarctica and to confirm the utility of this method as a source identification method. Sample extracts were purified and separated into several fractions by chromatographic and high performance liquid chromatographic

techniques to accurately measure the stable carbon isotope ratio of individual PAH compounds. The isolates were analyzed for PAH content as well. Stable carbon isotope ratios were measured by GC/IRMS and the results, along with quantitative compound distributions, were used to trace and identify the source of the detected contaminants. The stable isotopic compositions of the compounds of possible primary sources were determined. The stable isotopic compositions of contaminants from various locations were also measured. Traditional method to identify contaminant sources using compositional information was compared with the use of stable carbon isotopic signatures for source identification.

McMurdo Station is a major base for many field and research activities in Antarctica. Population at the station can exceed 1,000 during peak activity in the summer months (Mazzera *et al*., 1999). Human activities at McMurdo station have contributed to the contamination of terrestrial and adjacent marine habitats. Previous studies at McMurdo Station have documented several types of anthropogenic disturbances close to the station including petroleum hydrocarbons, chlorinated hydrocarbons, and metals (Kennicutt *et al*., 1995; Aislabie *et al*., 1999; Lyons *et al*., 1999; Mazzera *et al*., 1999). The hydrocarbon contamination is mostly near fuel tanks, fuel lines, landfills and helipads. This study focuses on areas of known impact in the vicinity of McMurdo Station. Samples from terrestrial and marine locations subject to a range of human activities were analyzed by stable carbon isotope methods.

Marine benthic sediments and soils were taken during mid-November through mid-December in 1999, 2000 and 2001. Sediment samples were taken by diver using hand-driven sediment cores (9-cm diameter). The top 0 – 3 cm sections of each core or surface soils were placed in clean 4 oz glass jars with Teflon lined lid. Soil samples were collected in the vicinity of McMurdo station including four sites of known contamination. The sites included fueling stations, old oil tanks, the helipad, and the machine shop. Marine sediment samples were collected at three stations along the coastline of McMurdo Station (Fig. 6.1). Samples were stored at – 20˚C until analysis.

Twenty-three soil samples and eleven marine sediment samples were analyzed for the

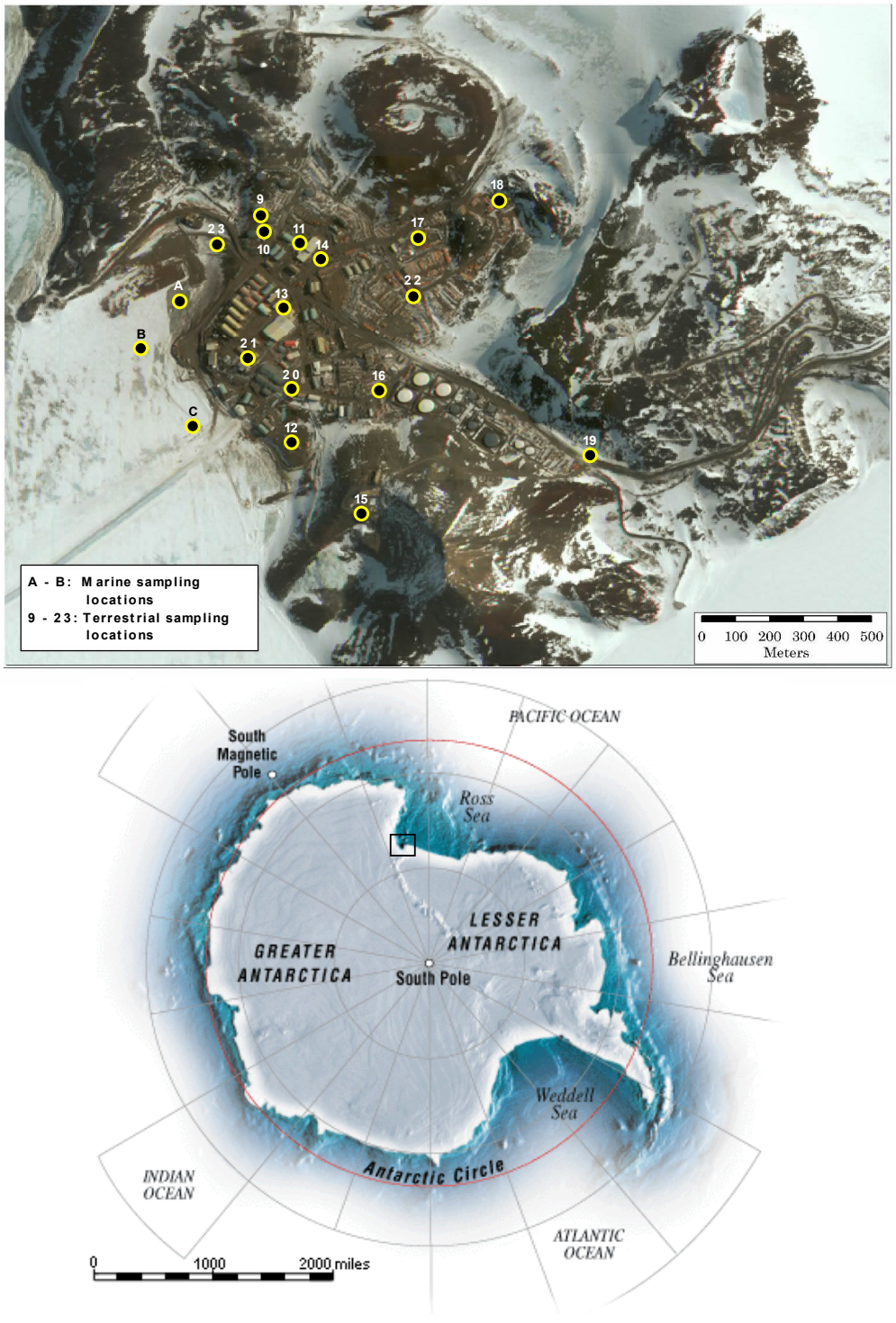


Fig. 6.1. Locations of sampling sites.

concentrations and the stable carbon isotope ratios of PAHs. Total PAH concentrations ranged from 664 ng/g to 74,267 ng/g dry wt for soil samples and from 621 ng/g to 5,024 ng/g dry wt for marine sediment samples (Table 6.1). Mean total PAHs in soils were 17,567 ng/g in 1999, 32,064 ng/g in 2000 and 19,750 ng/g in 2001 (Fig. 6.2) with no significant temporal trend during the study period. The lack of trend in soil PAH concentration is likely due to sampling design which included samples from remote sites in the 2001 sampling period. PAH contamination was relatively localized in areas where fuels were stored and used and in areas of heaviest traffic and parking in central McMurdo. Mean total PAHs for the samples from the four sites of known contamination sources increased by about a factor of two from 17,567 ng/g in 1999 to 38,326 ng/g in 2001 (Table 6.2). Changes in total PAH concentrations at each site are illustrated in Fig. 6.3. Changes in PAH were observed at the machine shop and fueling stations where on-going contamination is taking place. At the old oil tanks and the helipad, no significant change was detected during the study period. At the machine shop, contamination sources include crankcase oil, fuel, lubricants and emissions released during vehicle operation and repair. On-going introduction of fuel PAH at the fueling station and the machine shop was confirmed by changes in alkylnaphthalenes to total PAH ratios during the study period (Fig. 6.4). High alkylnaphthalenes to total PAH ratios infer that fresh or recent contamination from petroleum products has occurred. Increases of the ratios were detected at the fueling station and the machine shop samples, implying continued introduction of fresh fuel PAHs. Human activities involving the use of petroleum products introduce fuel PAHs to the environment.

Total PAH concentrations in marine sediments varied from 1,077 ng/g to 2,053 ng/g in 2000 sampling year and from 621 ng/g to 5,024 ng/g in 2001 sampling year. Highest concentrations were detected at station B in both sampling years. Mean total PAHs were 1,496 ng/g in 2000 and 2,322 ng/g in 2001. Although slight increases in total PAH were observed in marine sediments, the differences are likely the result of different sampling strategies. Sediments were collected at only three stations. The heterogeneity of PAH may account for between-year differences.

Table 6.1.
Total PAH concentrations at the study sites.

(ng/g dry wt.)

Year	Matrix	Average	Minimum	Maximum
1999	**Soil**	17,567	1,724	46,479
2000	**Sediment**	1,496	1,077	2,053
	Soil	32,064	3,807	74,267
2001	**Sediment**	2,322	621	5,024
	Soil	19,750	664	71,716

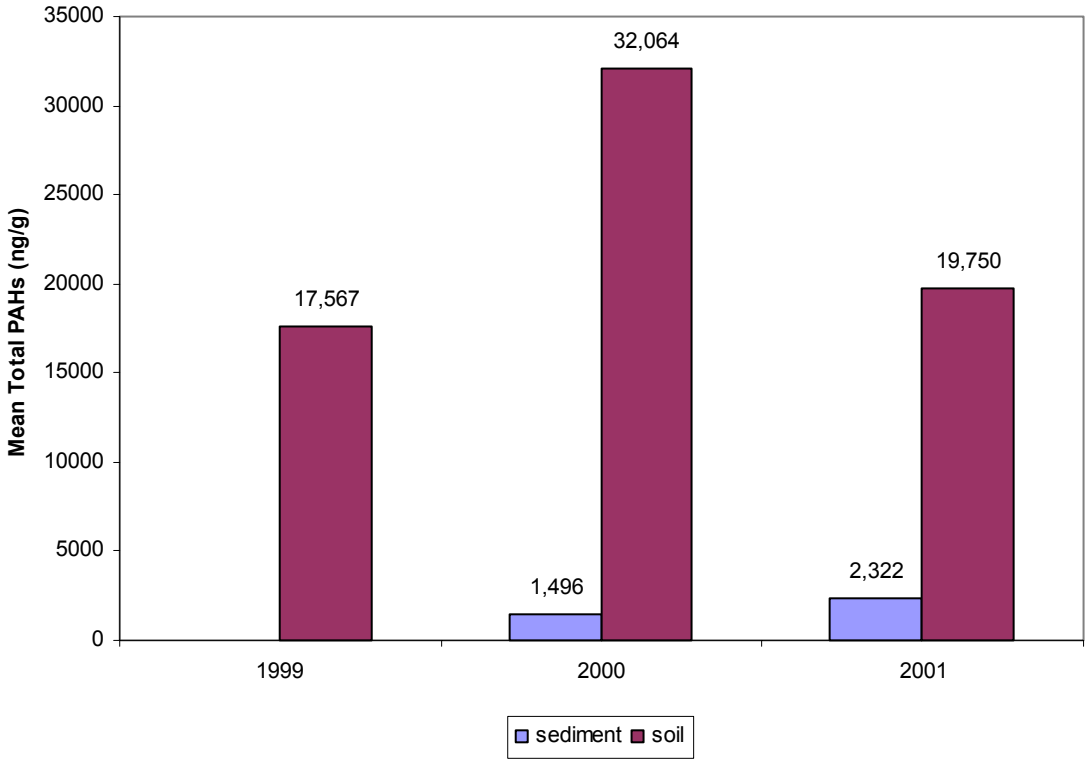


Fig. 6.2. Mean total PAH concentrations at the study sites.

Table 6.2.
Total PAH concentrations of soil samples at the four sites of known contamination.

(ng/g dry wt.)

Year	Matrix	Average	Minimum	Maximum
1999	**Soil**	17,567	1,724	46,479
2000	**Soil**	32,064	3,807	74,267
2001	**Soil**	38,326	9,690	56,645

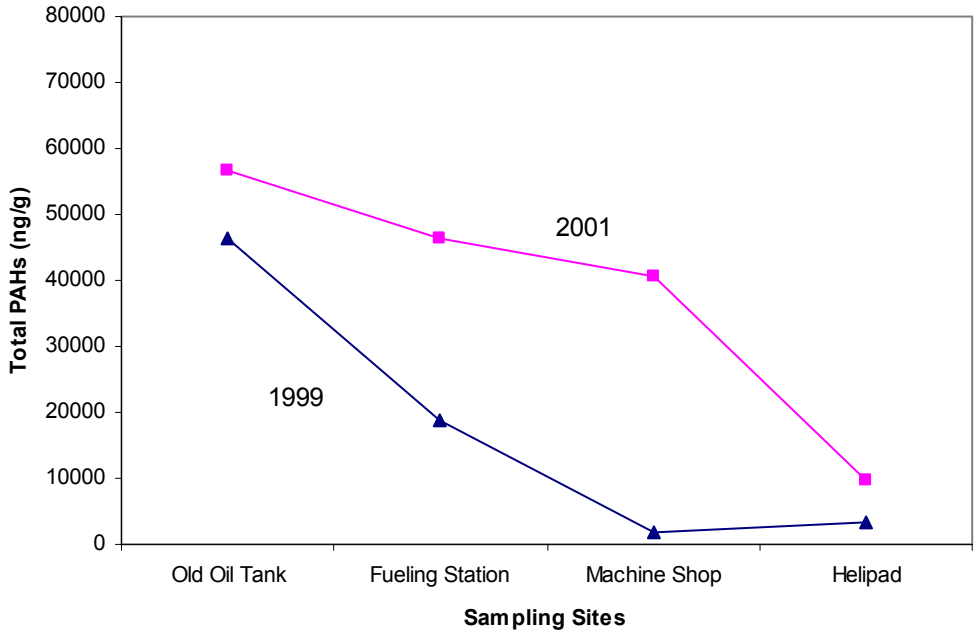


Fig. 6.3. Total PAH distributions showing changes in concentrations between 1999 and 2001 sampling years at the four sites of known contamination.

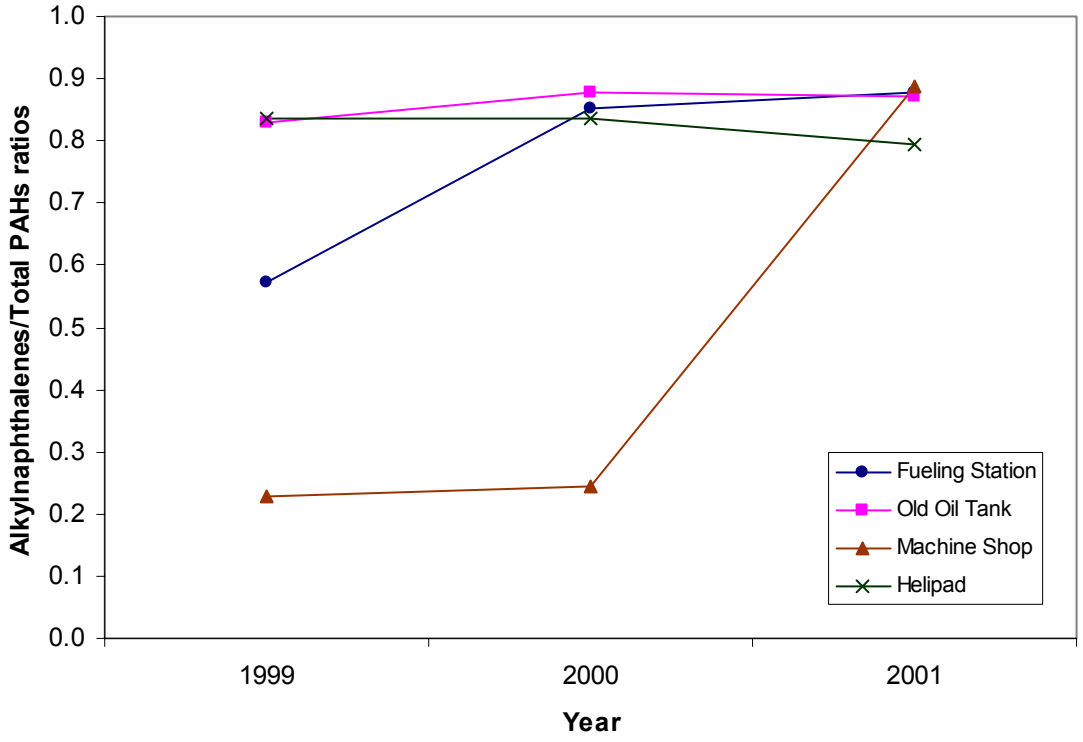


Fig. 6.4. Variations of alkylnaphthalenes / total PAH ratios at the four sites of known contamination during the study period.

The distribution of individual PAH compounds in selected samples is shown in Fig. 6.5. In most samples, alkylnaphthalenes were highest in concentration and accounted for the majority of the total PAH. Alkylated PAHs also increased in abundance with increased alkylation. In rare cases, the dominant PAHs were 3- to 4-ring PAHs (C in Fig. 6.5). Petrogenic PAHs derived from uncombusted petroleum products contain low molecular weight PAHs with one to three rings (Neff, 1979). They are characterized by homologous families of related PAHs such as, naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes, where alkylated PAHs for each family far exceed the unsubstituted parent PAHs (Lee *et al*., 1981; Page *et al*., 1999). Pyrogenic PAH are dominated by the parent compounds of the 3-, 4- and 5-ring PAHs. Fluoranthene and pyrene are usually considered major combustion derived PAH (Page *et al*., 1999; Witt and Trost, 1999). In this study, most of the PAHs in soils and sediments were petrogenic in origin as evidenced by the predominance of naphthalene and its alkylated compounds. Pyrogenic PAHs, such as fluoranthene and pyrene, were very low in concentration. They appear to be residues of combustion byproducts or residual weathered petroleum. Although some samples exhibited different distribution patterns (C in Fig. 6.5.) that had decreased abundances of alkylated naphthalenes, they do not appear to be pyrogenic in origin. Alkylnaphthalene distributions also suggest a petrogenic origin with a ratio of 0.9 of alkylnaphthalenes to total PAHs (Fig. 6.6).

PAH data were analyzed using Principal Component Analysis (PCA). The data analyzed included all measured parent and alkylated PAH homologues. The data matrix was standardized by subtracting the mean and dividing by the standard deviation. This standardization makes the centroid of the whole data set zero and assigns every variable a variance of 1.0 so that each variable has the same influence in the PCA. PCA was performed using the program SPSS 11.5 for Windows (SPSS Inc., Chicago, Illinois). Plots of principal component (PC) 1 and 2 of the total three extracted components are illustrated in Fig. 6.7. In the loading plot of the compounds, all petrogenic PAHs, like naphthalenes, fluorenes and phenanthrene, were positively loaded in PC 1, while high molecular weight PAH, mostly pyrogenic, were positively loaded in PC 2. No

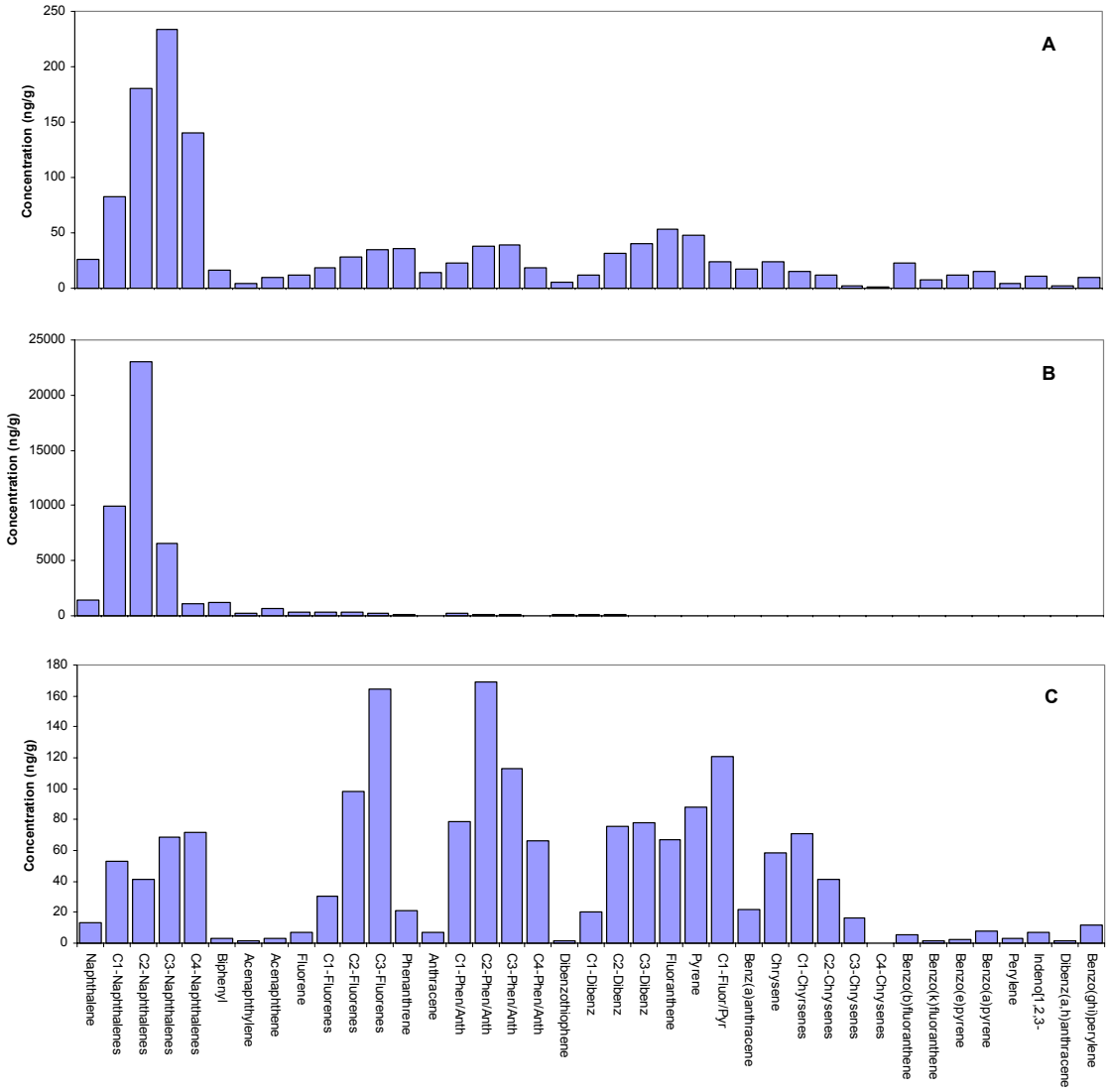


Fig. 6.5. PAH distribution patterns of selected samples (A: marine sediment (St. A, 2000), B: fueling station, 2001, C: storage area, 2001).

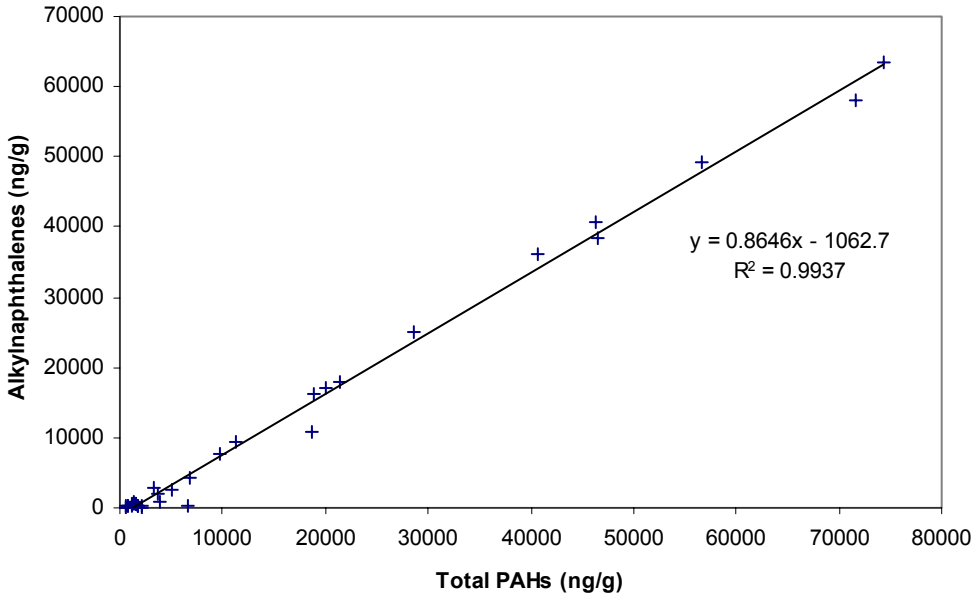


Fig. 6.6. Relationship between total PAHs and alkylnaphthalenes.

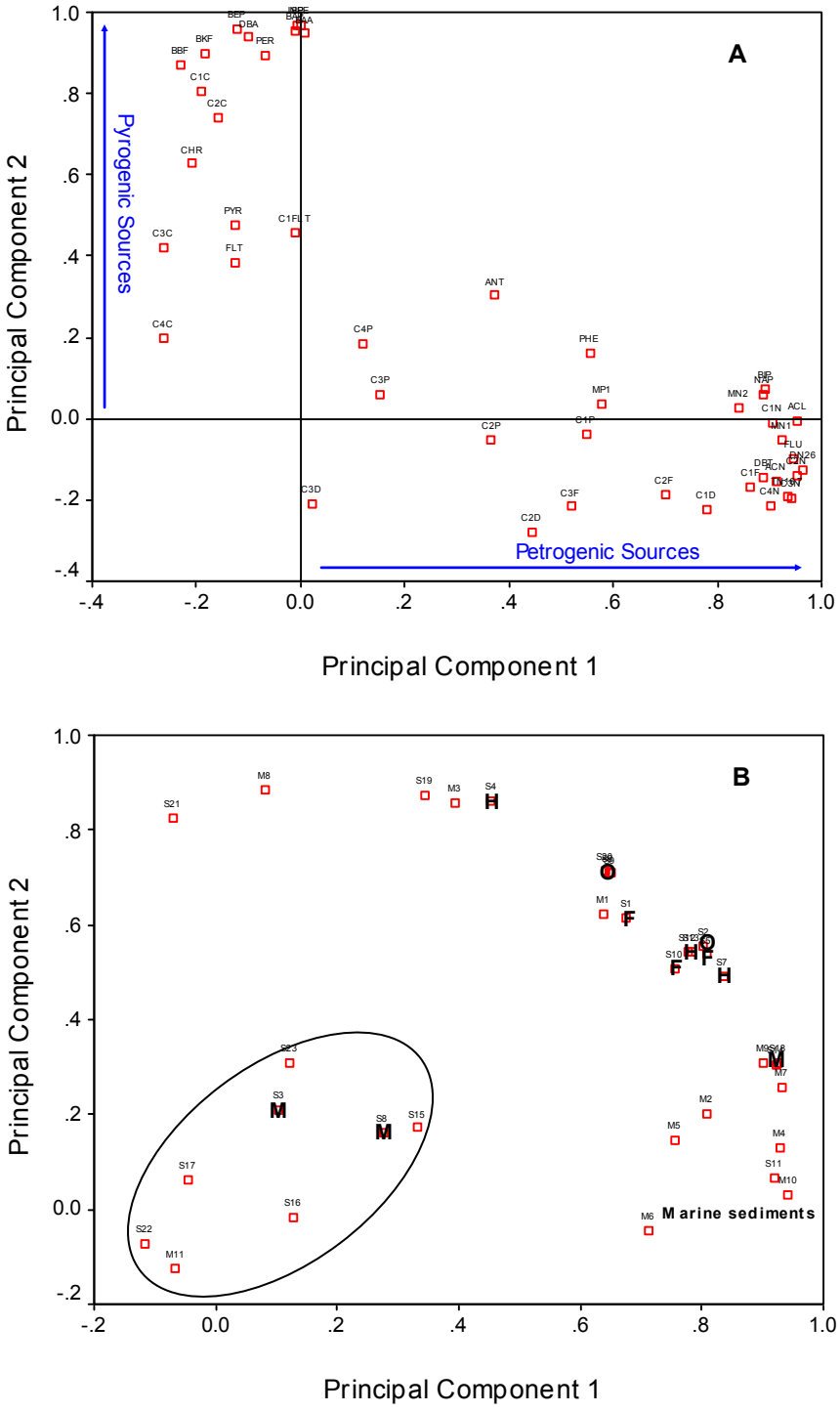


Fig. 6.7. Relationship between principal component 1 and principal component 2 for the principal component analysis of PAH data (above: PAH compounds, below: sampling sites, F: fueling station, O: old oil tank, M: machine shop, H: helipad).

relationship of petrogenic PAHs with PC 2 and pyrogenic PAHs with PC 1 implies that these two groups of PAHs have independent origins. This explains that naphthalene and alkylated naphthalenes, which are the majority of the PAHs in the samples originate from petroleum products, whereas other high molecular weight PAHs are related to combustion or emission sources.

In Fig. 6.7B, most of the marine sediment PAHs are explained by PC 1, while most of the soil samples include a significant portion related to PC 2. Most contamination at the fueling station (F), old oil tank (O), helipad (H) and machine shop (M) were positively loaded for both PC 1 and PC 2. Marine sediment samples, which are mostly explained by PC 1 and which showed low loading in PC 2, most likely originated from petrogenic sources which may be different from the petrogenic sources of the four terrestrial sites of known contamination. Winter Quarter Bay receives PAHs from several sources including fuels, lubricants, degraded petroleum residues not only by runoff from adjacent land areas, but also oil spills at the site. The soil samples in the lower left corner of the plot, including two machine shop (M) samples, showed little relationship with PC 1 and PC 2, implying distinctive source different from the sources for marine and other soil samples. All of the samples in the oval were collected at roadsides relatively remote from the suspected contamination sources. Most probable sources are emission from vehicle or direct release of hydrocarbons from the vehicle of unusual PAH sources such as lubricants. Those samples were also similarly loaded with two machine shop (M) samples related to the repair of vehicles. In addition, the samples were positively loaded in principal component 3. Although it is not clear what the governing factor for principal component 3 is, it is assumed that the principal component 3 may be contamination related to vehicles.

Highly degraded samples may exhibit compound compositions quite different from the original sources, making source identification difficult. Contaminants can be subjected to significant alterations once released to the environment. The alteration of original contaminant composition by physical, chemical, and biological processes can make it difficult to trace origins. Intrinsic tracers such as stable carbon isotope ratios are

one approach that may resolve pollutant sources in degraded samples. No significant isotopic fractionation of PAHs occurs during transportation in the environment (O'Malley *et al*., 1994), while biodegradation has an effect on the isotopic composition of the some low molecular weight PAHs, mostly alkylated naphthalenes, with a trend toward isotopic enrichment of the residual PAH material (Yanik *et al*., 2003). The stable carbon isotope ratios of PAHs in McMurdo soils and sediments are shown in Fig. 6.8. The stable carbon isotope ratios of naphthalene and methylnaphthalenes in marine sediments were more negative than those in soil samples, while stable carbon isotope ratios of higher molecular weight PAHs in marine sediments were enriched in ^{13}C relative to soil samples. Depletion of ^{13}C is the characteristics of samples which have petrogenic origins. Strong petrogenic inputs of naphthalene and methylnaphthalenes to the marine sediment samples are recognizable.

The stable carbon isotope ratios of naphthalene and methylnaphthalenes from the four sites of known contamination are shown and compared with those of marine sediment in Fig. 6.9. The fueling station, the old oil tanks, and the helipad exhibit similar isotope ratios, implying a common origin for the PAHs. However, machine shop samples exhibited clearly different stable carbon isotope ratios the more depleted in ^{13}C. At the fueling station, the old oil tanks and the helipad, major contamination source is fuel. At the machine shop, however, contamination sources not only include fuel, but also crankcase oil, lubricants and other emissions related with vehicle repair. Marine sediments showed much more depletion than machine shop. This may infer distinct sources for the naphthalene and methylnaphthalenes in marine sediment samples. Marine sediments were more depleted in ^{13}C compounds and can not be explained solely by inputs from the four contamination sources. Marine sediments are exposed to the long term accumulation from various contamination sources. Many kinds of spills, including petroleum hydrocarbon have been reported in the Winter Quarter Bay area over many years (Kennicutt *et al*., 1995; Aislabie *et al*., 1999; Lyons *et al*., 1999; Mazzera *et al*., 1999). The stable carbon isotope ratios of marine sediment PAH are likely the result of direct spills or ship operations in the Winter Quarter Bay as well as from the run off

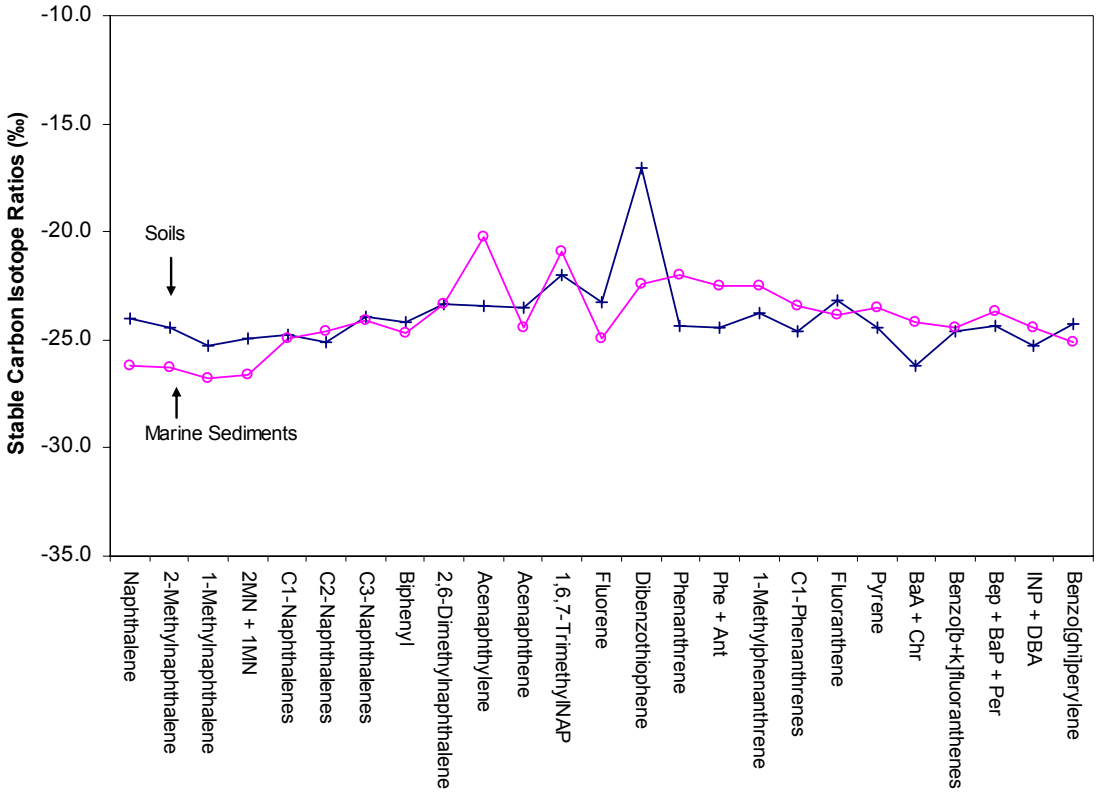


Fig. 6.8. Mean stable carbon isotope ratios of PAHs at the study sites.

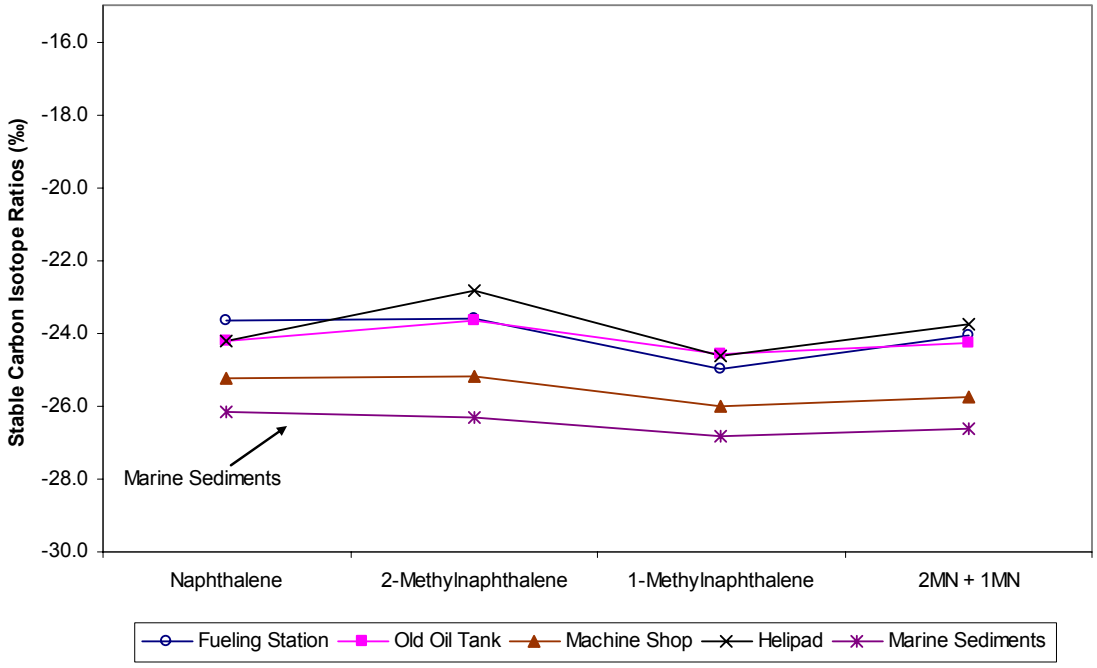


Fig. 6.9. Mean stable carbon isotope ratios of selected PAHs measured at the four sites of known contamination and comparison with marine sediments (2MN: 2-methylnaphthalene, 1MN: 1-methylnaphthalene).

from the adjacent land areas.

Due to the lack of stable isotope ratios for other possible sources for marine sediment PAHs and due also to the low concentrations of PAHs for isotope ratio measurement in the other soil samples except four possible contamination sources, direct comparison of stable isotope ratios between samples and possible sources or quantitative source apportionment using mass balance equation are difficult at best. For clearer source identification and apportionment, isotopic signature of the sources should be well defined and enough materials must be recovered from the samples for accurate measurement of stable carbon isotope ratios.

In this study, marine sediment and soil samples from the McMurdo Station are characterized by their high relative proportion of naphthalene and alkylated naphthalenes from fuel sources. Distinctive source for the marine sediment PAHs were confirmed by the principal component analysis of PAH data and also by stable carbon isotope analysis. Marine sediment PAHs were clearly different from the petrogenic sources of the four sites of known contamination. Some soil samples collected at roadsides remote from fuel contamination sources showed distinctive sources different from the sources for marine sediments and other soil samples. Most of the PAH contamination was due to fuel consumption and distributions were localized. The PAHs likely persist in the area because of the cold temperatures, low microbial activity and continued human activities at the sites. There is potential for PAHs to be transported to the marine environment by runoff and atmospheric deposition.

Compound distribution pattern and compound molecular ratios can be applied for source identification of contaminants in the environment. However highly degraded samples may exhibit compound composition quite different from the original sources, making source identification difficult. Stable carbon isotope ratios, which are relatively resistant to environmental degradation, can support molecular methods and can be an effective alternative to traditional molecular methods. This study confirms that the developed purification and compound specific stable carbon isotope analysis methods can be used to differentiate PAH mixtures in the environment.

CHAPTER VII

SUMMARY AND CONCLUSIONS

Purification and compound specific stable carbon isotope analysis methods for PAHs were developed. The purification method includes alumina/silica gel column chromatography, gel permeation chromatography and thin layer chromatography. Thin layer chromatography can be replaced with carbon/silica gel chromatography if fewer planar impurities, like dioxins or planar PCBs, are present. PAHs are separated from impurities during the purification steps based on the polarity, molecular size and planar structure of PAHs and a PAH band is finally recovered from the TLC plate. To increase the recovery of high molecular weight PAHs on carbon/silica gel column chromatography, column reversal technique was used. The TLC method uses cyclohexane/toluene (3/2) development in an unsaturated chamber environment to achieve the cleanest separations. The low recoveries of low molecular weight PAHs from TLC separations are most likely due to evaporation. The mean recovery of PAHs after the purification procedure was about 80 %. Although lower recoveries were seen for low molecular weight PAHs, especially for naphthalene (50 %), no isotopic fractionation occurred during purification. Sample purities after purification were verified by GC/FID and full scan mass spectrometry.

To better resolve peaks and provide more accurate stable isotope results, various gas chromatographic conditions were tested. To improve the accuracy of the isotopic analyses, peak resolution, signal linearity, system stability, sensitivity, and peak flatness were tested. For individual compounds, method precision ranged between 0.08 and 0.43 ‰. Precision increases with peak intensity because the contribution of background or interfering materials is greater for small peaks. Method accuracy was confirmed with standard materials. The analytical protocols were evaluated to confirm compositional and stable isotopic integrity during purification. While most compounds exhibited isotopic conservation during purification, some compounds exhibited some isotopic

enrichment during purification, which may be caused by the preferential loss of isotopically light PAH during evaporation. However, measured isotopic ratios for purified standards fall within two standard deviations (2σ) of the mean isotope ratio of unprocessed standard material, with one exception of the combined peaks of benzo[e]pyrene, benzo[a]pyrene, and perylene, which require the use of a correction factor.

There are several conclusions about the purification and isotope analysis procedures.

- The amount of sample to be extracted should be determined based on the PAH concentration data in order for peak response to fall within the linearity range of IRMS response.
- The amount of pentane to elute the aliphatic fraction from alumina (10g, 1% H_2O) / silica (20g, 5% H_2O) columns should be increased to 100 ml to maximize the purification step.
- In order to reduce evaporative losses during thin layer chromatography, application time should be minimized and a minimum amount of solvent should be used to apply the sample to the plate.
- For precise isotopic analyses, the relationship between precision and peak size should be used to establish a minimum peak size for analysis.
- Higher GC head pressure can be helpful in improving peak resolution but it may cause losses in signal sensitivity.
- Inlet purge time should be adjusted if solvent tailing is noticeable in splitless inlet systems to improve the accuracy of isotope ratio measurements.

The purification and isotope analysis methods were used to analyze the sediments from an urban lake in the northwestern U.S. PAHs in the urban lake sediments are characterized by the high concentrations, up to a percent level, their pyrogenic origins, and the distinctive molecular and isotopic signatures. The uniqueness of the source of the sediment PAHs is illustrated by PAH molecular ratios and confirmed by stable

carbon isotope ratios. The pyrogenic properties most likely originate from the coal gasification processes that occurred in the area for more than 50 years. The constancy of molecular ratios and stable carbon isotope ratios over the sampling period of 3 years confirmed that the source in the study sites were the same and probably occurred sometime in the past. The higher variability of stable carbon isotope ratios for some low molecular weight PAHs indicated multiple sources for the compounds and varying degrees of degradation. Naphthalene and methylnaphthalenes were enriched in heavy isotopes over time. This enrichment may be the result of biodegradation or physicochemical processes such as evaporation which involve kinetic isotopic fractionation or isotope exchange effects, respectively (Hoefs, 1997).

In order to confirm the applicability of the developed purification and isotope analysis methods, samples from Antarctica were also analyzed for their composition and the stable carbon isotope ratios of PAHs. Marine sediment and soil samples from the McMurdo Station are characterized by their high relative proportion of naphthalene and alkylated naphthalenes from fuel sources. Naphthalene and alkylnaphthalenes had petrogenic origins as seen by their compositional patterns. On-going introduction of fresh fuel at certain sites was confirmed by changes in alkylnaphthalenes to total PAH ratios. Human activities involving the use of petroleum products introduce fuel to the environment. Distinctive source for the marine sediment PAHs were confirmed by the principal component analysis of PAH data and also by stable carbon isotope analysis. Marine sediment PAHs were much more depleted in ^{13}C and have strong petrogenic inputs that can not be explained by the inputs from the petrogenic PAHs from the shore. There is a history of spills in the Winter Quarter Bay area. The low stable carbon isotope ratios of marine sediments are likely the result of direct spills, instead of the four contamination sources on the adjacent land. Some soil samples collected at roadsides remote from fuel contamination sources showed distinctive composition different from the marine sediments and other soil samples. The most probable sources are emission from vehicle or the direct release of hydrocarbons such as lubricants.

The purification and analysis methods for the compound specific stable carbon isotope measurement provided good compound recovery, peak resolution and sensitivity, and precise and accurate isotopic ratios. However, the GC/IRMS system requires high concentrations for reliable isotope ratio analysis. At least 10 ng per each PAH peak which is about 5 ng/µl of individual PAH in final solution is needed, if 2 µl of sample is injected. This may require the extraction of large amounts of samples. Extraction of large amount of sediments may require extensive purification steps, making the method impractical for low concentration samples. Development of more sensitive isotope analysis methods or more sensitive IRMS system may solve this problem.

The GC is linked with IRMS through an interface consisting of a combustion furnace, a water removal system and an open split. They are connected by various tubing and connectors which can create dead volume causing tailing and broadening of chromatographic peaks. Even after an effort to reduce peak broadening caused by numerous connections, several peaks could not be resolved to baseline-separation. The peaks include phenanthrene-anthracene, benz[a]anthracene-chrysene, and benzo[b]fluoranthene-benzo[k]fluoranthene. Baseline-separation is essential for accurate and precise isotope ratio analysis. The problem can be overcome by modifying the configuration of interface system. Modification may include reducing the number of connections, adopting a capillary combustion furnace instead of ceramic furnace (Ellis and Fincannon, 1998), minimizing dead volume by replacing connections with dead-volume-free connections, and simplifying the interface system.

Compound distribution pattern and compound molecular ratios can be used for source identification in the environment. However highly degraded samples may exhibit compound composition quite different from the original sources, making source identification difficult. Stable carbon isotope ratios, which are relatively resistant to environmental degradation, can be an additional tool used in conjunction with traditional molecular methods to trace contaminants. This study confirms that compound specific isotope analysis of pollutant extracts by gas chromatography linked with an isotope ratio mass spectrometer can be used to identify PAH origins in natural samples. The study

also confirms that the developed purification and compound specific stable carbon isotope analysis methods can be effectively used to accurately measure the stable carbon isotope ratios of PAHs in environmental samples for the purposes of source identification. These methods are applicable to environmental samples of soil, sediment and possibly water and atmospheric samples as long as sufficient amounts of contaminants are present.

The developed method has not been checked systematically with tissue samples which may have increased interferences from lipids. Although some tissue samples were tested and showed good purification during the development, the method should be systematically validated for tissue samples.

Environmental contaminations are the result of complex mixtures from multiple sources. Quantitative source apportionment may be possible using a mass balance approach if end members are well-defined. Stable carbon isotope ratios are one possible variable that could be used for a mass balance approach because of their resistance to environmental alteration. Methods should be applied to pollutant scenarios of known multiple inputs to verify the validity of the method.

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APPENDIX

Table A.1.
List of PAH compounds analyzed.

	No. of rings	MW[a]	QI[b]	CI[c]	MDL[d]
Naphthalene	2	128	128	127	0.26
C1-Naphthalenes	2	142	142	141	0.84
C2-Naphthalenes	2	156	156	141	0.22
C3-Naphthalenes	2	170	170	155	0.45
C4-Naphthalenes	2	184	184	169	0.45
Biphenyl	2	154	154	153	0.18
Acenaphthylene	3	154	152	153	0.25
Acenaphthene	3	154	154	153	0.44
Fluorene	3	166	166	165	0.22
C1-Fluorenes	3	180	180	165	0.45
C2-Fluorenes	3	194	194	179	0.45
C3-Fluorenes	3	208	208	193	0.45
Phenanthrene	3	178	178	176	0.22
Anthracene	3	178	178	176	0.24
C1-Phe/Ant	3	192	192	191	0.43
C2-Phe/Ant	3	206	206	191	0.43
C3-Phe/Ant	3	220	220	205	0.43
C4-Phe/Ant	3	234	234	219	0.43
Dibenzothiophene	3	184	184	152	0.14
C1-Dibenzothiophenes	3	198	198	184	0.29
C2-Dibenzothiophenes	3	212	212	197	0.29
C3-Dibenzothiophenes	3	226	226	211	0.29
Fluoranthene	4	202	202	101	0.39
Pyrene	4	202	202	101	0.45
C1-Flu/Pyr	4	216	216	215	0.84
Benz[a]anthracene	4	228	228	226	0.23
Chrysene	4	228	228	226	0.27
C1-Chrysenes	4	242	242	241	0.54
C2-Chrysenes	4	256	256	241	0.54
C3-Chrysenes	4	270	270	255	0.54
C4-Chrysenes	4	284	284	269	0.54
Benzo[b]fluoranthene	5	252	252	253	0.25
Benzo[k]fluoranthene	5	252	252	253	0.22
Benzo[e]pyrene	5	252	252	253	0.23
Benzo[a]pyrene	5	252	252	253	0.39
Perylene	5	252	252	253	0.55
Dibenzo[a,h]anthracene	5	278	278	279	0.16
Indeno[1,2,3-cd]pyrene	6	276	276	277	0.32
Benzo[ghi]perylene	6	276	276	277	0.30
2-Methylnaphthalene	2	142	142	141	0.47
1-Methylnaphthalene	2	142	142	141	0.36
2,6-Dimethylnaphthalene	2	156	156	141	0.11
1,6,7-Trimethylnaphthalene	2	170	170	155	0.23
1-Methylphenanthrene	3	192	192	191	0.21

Table A.1.
Continued.

	No. of rings	MW[a]	QI[b]	CI[c]	Note
d10-Fluorene	3	176	176	174	Recovery IS
d12-Benz[a]pyrene	5	264	264	260	Recovery IS
d8-Naphthalene	2	136	136	134	Surrogate IS
d10-Acenaphthene	3	164	164	162	Surrogate IS
d10-Phenanthrene	3	188	188	184	Surrogate IS
d12-Chrysene	4	240	240	236	Surrogate IS
d12-perylene	5	264	264	260	Surrogate IS

a: Molecular weight, b: Quantification ion, c: Confirmation ion, d: Method detection limit (ng/g)

Table A.2. Concentrations (ng/g) of PAHs in sediment samples for Chapter V.

Sample Identification	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Sampling Date	7/28/2000	7/28/2000	7/28/2000	7/28/2000	7/28/2000	7/28/2000	7/31/2000	7/31/2000	7/31/2000	7/31/2000	7/31/2000	7/31/2000	7/31/2000	7/31/2000	6/27/2001	6/27/2001
Sampling Location	Shipping Waterway	Shipping Waterway	Shipping Waterway	Harbor	Harbor	Harbor	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake
Naphthalene	198.1	42.1	171.9	1,310.0	307.9	283.2	3,673.1	63,669.9	30,318.0	75,114.5	54,903.7	33,802.7	85,733.2	9,353.1	15,820.9	43,346.8
C1-Naphthalenes	168.4	51.1	144.6	316.5	211.0	174.7	1,849.9	36,855.4	11,119.6	16,162.3	11,539.2	8,477.5	22,068.9	2,118.8	4,064.0	16,061.2
C2-Naphthalenes	189.5	107.1	124.8	227.1	190.4	121.4	1,547.2	37,201.9	11,028.6	14,968.1	8,134.7	3,888.6	19,420.3	1,898.1	2,249.7	12,275.1
C3-Naphthalenes	179.3	85.8	137.7	135.4	138.5	75.8	1,341.3	43,152.7	18,912.1	19,112.0	10,483.3	3,811.1	22,828.1	1,376.7	2,095.8	12,216.5
C4-Naphthalenes	125.4	83.6	112.0	109.8	68.4	49.3	636.0	24,365.5	12,220.2	9,616.5	5,935.2	2,770.6	12,249.6	768.1	1,518.2	5,293.9
Biphenyl	43.9	13.5	20.5	104.1	41.8	39.8	517.2	8,064.5	4,964.0	15,312.2	9,515.2	6,017.8	16,231.4	1,732.3	2,730.6	8,231.3
Acenephthylene	129.9	32.6	64.2	293.9	208.6	216.3	998.3	23,352.6	24,482.6	22,086.9	15,139.1	11,280.2	25,354.7	3,061.0	6,010.9	23,618.8
Acenaphthene	387.7	105.8	78.9	358.0	147.0	166.5	1,384.9	32,919.1	18,880.4	148,960.2	61,211.0	22,442.7	115,206.1	35,587.8	11,765.6	98,066.0
Fluorene	611.6	110.9	104.4	538.5	319.1	319.6	1,203.8	27,868.4	17,078.6	80,223.8	35,840.4	12,274.3	65,799.3	11,148.0	5,704.5	42,376.0
C1-Fluorenes	201.3	61.8	66.9	507.7	142.9	126.7	796.9	25,764.9	18,759.9	22,469.1	12,662.1	4,289.1	19,824.0	1,223.0	2,462.6	11,483.9
C2-Fluorenes	272.0	-	280.5	906.1	236.0	166.9	762.5	28,559.2	25,392.5	16,567.8	10,819.3	4,564.7	16,444.8	1,438.8	2,473.3	9,365.1
C3-Fluorenes	238.5	245.8	193.2	1,195.1	268.7	270.0	565.4	19,407.0	16,293.0	11,602.6	7,506.4	4,295.3	13,087.2	1,228.2	2,332.6	7,339.1
Phenanthrene	1,543.0	419.7	514.0	1,207.9	953.2	734.3	5,450.1	148,464.9	108,252.7	528,131.8	227,732.1	57,993.8	560,852.6	28,048.5	35,489.8	168,860.3
Anthracene	1,492.4	501.9	367.6	3,439.2	1,913.8	1,840.4	2,293.1	75,624.1	61,717.8	263,101.0	111,145.0	30,586.6	236,340.4	8,595.3	14,756.4	83,467.4
C1-Phen/Anth	759.2	324.1	307.0	1,687.1	862.3	587.9	3,069.7	105,774.4	92,601.0	95,298.3	53,929.0	18,792.1	92,468.6	4,298.0	9,588.7	46,838.8
C2-Phen/Anth	511.7	260.3	278.3	1,680.7	555.1	423.0	2,283.0	85,819.2	62,764.3	38,429.1	25,727.1	12,666.4	38,934.8	2,891.8	6,408.6	26,545.3
C3-Phen/Anth	332.5	267.3	231.4	991.6	293.5	286.8	1,345.1	53,605.0	25,140.8	14,232.1	10,992.3	5,951.2	15,000.7	1,682.8	6,465.9	13,706.1
C4-Phen/Anth	174.9	184.7	172.5	431.1	166.9	180.4	646.2	27,205.7	6,999.7	3,843.3	3,855.8	2,199.1	4,977.7	801.7	12,692.5	7,884.0
Dibenzothiophene	115.8	42.2	46.6	116.1	69.2	53.5	713.0	20,135.9	14,947.6	101,339.1	44,553.6	14,153.9	82,485.5	5,180.2	6,082.7	35,198.8
C1-Dibenz	66.5	36.8	48.0	96.6	62.7	33.2	498.1	15,816.6	14,654.5	19,255.6	10,614.2	4,440.1	17,744.7	1,005.8	2,299.8	9,312.6
C2-Dibenz	69.3	100.4	74.4	261.1	65.0	49.9	384.9	13,160.4	14,594.2	9,971.3	5,986.5	3,507.0	10,475.8	969.5	1,753.1	6,949.3
C3-Dibenz	135.5	556.9	290.2	253.6	140.8	166.1	246.0	7,308.1	8,321.0	4,724.5	3,027.8	2,110.4	5,877.7	860.8	1,028.7	4,322.5
Fluoranthene	4,475.3	2,282.2	1,575.1	13,793.2	1,587.3	1,912.7	14,264.8	267,218.7	252,268.4	781,108.4	430,189.1	255,728.1	814,213.8	61,754.9	127,219.3	426,804.7
Pyrene	3,427.2	3,557.2	1,614.4	12,755.9	4,520.3	5,033.7	16,994.6	309,749.8	301,018.4	907,035.5	514,266.5	308,176.1	973,085.7	73,651.6	153,884.7	521,071.0
C1-Fluor/Pyr	2,577.0	1,938.0	836.1	8,440.0	3,407.4	3,298.0	4,011.7	127,425.2	131,174.2	158,949.2	95,075.0	53,127.7	158,896.9	11,914.0	26,519.5	106,377.6
Benz(a)anthracene	2,099.8	1,248.7	549.8	4,707.4	2,221.7	2,163.5	5,763.0	129,025.4	119,971.0	286,602.2	164,149.1	95,551.4	290,052.4	21,688.8	43,380.4	163,741.2
Chrysene	3,190.0	3,235.9	1,352.7	4,239.8	3,366.2	3,244.2	6,165.9	121,356.5	115,907.3	247,058.3	159,502.7	94,808.2	300,913.9	24,681.4	45,402.9	159,169.9
C1-Chyrsenes	779.6	820.8	412.7	2,202.5	1,312.6	1,221.4	1,770.1	59,574.6	54,172.4	49,048.2	33,113.6	20,074.9	52,766.4	5,029.7	9,841.4	44,195.9
C2-Chrysenes	281.8	253.0	233.2	569.2	396.2	372.7	531.9	22,649.9	16,833.0	12,545.7	8,892.5	5,054.8	13,887.1	1,586.1	2,350.4	12,910.5
C3-Chrysenes	21.8	33.9	32.3	23.9	18.0	15.8	42.8	1,759.4	766.8	591.4	447.9	314.3	589.5	192.7	151.4	665.9
C4-Chrysenes	63.5	85.1	41.6	95.7	73.9	67.1	170.7	3,644.7	3,070.2	7,474.7	4,480.9	2,467.0	7,612.3	638.9	1,058.0	4,625.6
Benzo(b)fluoranthene	2,868.6	3,484.1	1,424.8	4,358.3	2,938.4	3,011.5	8,482.2	185,161.8	151,374.8	366,663.6	214,083.0	143,406.3	395,787.0	35,600.8	61,924.4	225,353.9
Benzo(k)fluoranthene	982.5	1,004.3	357.0	1,149.7	1,106.2	1,017.3	3,780.3	36,955.4	45,713.2	90,316.9	67,073.8	43,445.6	126,469.6	16,470.7	23,562.2	68,403.3
Benzo(e)pyrene	1,391.1	1,910.8	762.3	1,811.0	1,321.2	1,305.1	6,375.6	112,802.8	101,580.1	227,157.0	142,276.9	99,286.0	269,215.4	27,297.1	43,937.8	151,236.1
Benzo(a)pyrene	2,224.1	1,649.3	779.3	3,525.8	2,478.4	2,186.0	14,232.7	260,745.3	247,307.7	554,825.8	340,250.8	230,388.6	638,158.4	62,464.5	101,107.2	340,764.1
Perylene	479.0	299.9	202.8	521.1	468.0	602.1	2,721.9	43,178.0	41,281.6	100,715.7	61,386.3	42,856.3	114,037.6	11,286.9	18,485.5	64,247.8
Indeno[1,2,3-cd]pyrene	903.9	850.9	367.2	936.6	681.8	579.4	7,916.6	153,592.1	140,571.2	336,176.8	200,684.3	138,819.2	397,788.2	34,444.4	58,287.6	213,125.5
Dibenz(a,h)anthracene	199.5	222.7	89.5	257.5	190.8	154.9	439.7	15,126.4	10,616.2	27,709.2	17,645.7	8,031.0	26,189.2	1,863.6	3,167.8	18,483.0
Benzo(ghi)perylene	776.8	934.3	380.8	743.5	532.4	461.9	8,755.7	154,381.5	140,824.0	329,497.6	201,620.0	144,083.4	394,052.0	37,950.7	62,647.4	224,946.5
Total PAHs	**34,688.2**	**27,445.4**	**14,841.1**	**76,298.2**	**33,983.2**	**33,012.9**	**134,625.7**	**2,928,442.7**	**2,493,893.9**	**6,013,998.1**	**3,396,391.0**	**1,955,933.8**	**6,473,121.2**	**553,785.1**	**938,722.2**	**3,438,880.9**
Specific Isomers																
2-Methylnaphthalene	103.9	31.2	95.9	151.1	129.9	103.5	901.8	19,554.5	6,896.8	9,683.7	7,195.8	5,522.5	14,198.2	1,435.4	2,500.7	9,169.7
1-Methylnaphthalene	64.5	19.9	48.7	165.4	81.1	71.3	948.1	17,300.9	4,222.8	6,478.6	4,343.4	2,954.9	7,870.7	683.4	1,563.3	6,891.5
2,6-Dimethylnaphthalene	123.7	86.8	66.6	166.4	116.0	94.3	713.0	15,990.1	4,897.0	7,029.5	3,832.5	2,077.8	9,649.8	781.9	969.6	4,769.4
1,6,7-Trimethylnaphthalen	67.8	29.0	52.1	40.9	42.6	23.1	417.8	14,131.0	4,946.7	5,502.5	2,880.7	1,188.3	6,117.8	430.0	670.6	3,160.0
1-Methylphenanthrene	201.6	80.9	126.4	548.0	236.2	170.6	1,050.9	34,258.2	26,203.7	25,294.5	14,436.4	5,480.1	22,134.0	1,161.1	3,069.3	12,911.0

Table A.2. Continued.

Sample Identification	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Sampling Date	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	6/27/2001	3/15/2002	3/15/2002	3/15/2002	3/15/2002
Sampling Location	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake
Naphthalene	95,150.1	90,913.8	35,471.4	29,372.5	455,811.0	78,580.1	43,474.9	80,103.4	65,519.3	64,738.3	84,883.6	30,076.8	17,528.2	18,507.7	13,253.4	4,027.4
C1-Naphthalenes	32,235.7	27,046.1	8,853.3	7,131.2	108,693.6	27,817.7	14,404.9	54,640.3	15,715.0	12,659.8	85,594.8	24,527.7	11,049.7	4,869.6	3,182.2	1,235.7
C2-Naphthalenes	44,688.1	19,625.4	6,552.2	3,385.9	62,960.8	26,420.2	10,700.8	62,652.6	19,941.9	14,411.0	119,246.0	22,294.0	12,772.6	3,464.2	2,103.0	728.4
C3-Naphthalenes	49,335.8	23,364.2	5,950.2	2,995.7	52,575.3	25,299.2	19,445.3	69,546.8	22,944.2	26,485.2	96,516.6	19,112.9	8,584.1	4,014.9	5,340.3	844.6
C4-Naphthalenes	21,216.1	13,239.0	3,520.9	2,538.1	22,552.6	12,347.0	13,047.5	30,053.4	11,274.6	16,529.7	37,536.2	8,424.3	4,338.0	2,237.9	5,158.2	719.5
Biphenyl	17,866.2	15,876.1	6,503.4	5,623.8	107,595.0	18,471.0	9,034.5	13,191.8	12,797.1	10,198.5	13,253.7	5,418.0	3,169.4	3,368.9	1,756.2	645.7
Acenephthylene	24,961.4	30,431.9	11,756.2	9,402.8	227,234.8	21,226.8	15,263.2	27,039.2	23,654.8	14,559.6	25,263.4	11,222.9	6,847.1	5,616.4	3,307.3	1,298.2
Acenaphthene	180,812.1	106,651.8	47,790.4	23,249.4	648,326.3	82,536.1	21,088.0	87,352.6	56,394.5	39,679.6	114,319.3	35,387.9	23,223.7	40,708.8	3,243.8	2,307.3
Fluorene	124,389.3	66,409.4	25,773.6	11,641.0	266,026.5	63,212.6	22,838.8	74,076.0	42,932.5	36,218.6	96,400.3	27,543.8	16,008.3	14,738.4	2,867.4	1,314.3
C1-Fluorenes	37,499.0	21,690.9	5,553.4	3,331.8	53,192.1	19,784.4	14,367.4	40,923.8	16,897.3	17,515.3	53,678.1	12,041.5	5,952.1	3,513.9	4,238.5	815.6
C2-Fluorenes	26,472.3	18,677.1	4,648.7	3,494.2	36,423.6	17,754.4	16,066.8	37,181.7	14,624.2	17,907.5	45,291.1	10,966.0	5,290.6	3,110.0	5,323.1	950.9
C3-Fluorenes	17,806.8	15,526.4	4,461.2	3,363.6	26,328.5	12,861.8	12,668.9	25,445.6	11,370.8	14,192.1	28,396.1	8,461.6	4,570.9	2,842.9	4,604.8	974.0
Phenanthrene	1,076,539.4	521,915.7	79,905.8	37,427.2	1,566,261.0	444,499.5	240,034.7	518,508.8	401,304.5	351,809.0	638,214.1	155,137.0	62,671.7	58,072.8	22,832.6	4,120.5
Anthracene	544,026.1	350,324.2	32,657.2	17,675.5	764,979.8	199,996.3	133,780.3	311,418.8	234,790.6	187,577.1	368,184.9	74,788.5	39,370.9	28,210.5	20,882.1	3,521.2
C1-Phen/Anth	173,605.8	107,064.0	17,693.6	10,183.1	223,620.6	92,516.0	64,647.6	164,210.3	74,261.6	81,416.4	197,054.6	46,408.0	19,514.9	13,028.0	14,347.1	1,908.3
C2-Phen/Anth	60,226.6	47,274.0	11,956.4	8,066.8	81,550.4	41,553.9	33,719.3	85,323.0	31,128.9	38,819.1	94,679.0	24,824.4	11,942.6	7,105.6	11,187.0	2,032.2
C3-Phen/Anth	21,671.2	19,637.7	6,165.6	4,254.0	27,900.1	16,216.2	15,206.2	31,176.6	12,051.1	15,687.0	32,937.0	10,536.8	6,025.7	3,299.9	5,374.0	1,448.5
C4-Phen/Anth	7,684.7	6,269.1	3,426.2	1,800.9	7,046.4	4,553.5	4,420.4	7,682.4	3,257.9	6,743.0	7,659.3	3,209.6	4,217.0	1,147.7	1,926.4	748.7
Dibenzothiophene	158,736.1	75,094.7	23,078.0	9,471.6	288,664.6	67,876.8	38,394.4	70,130.6	54,630.0	51,327.5	84,890.8	21,785.6	12,061.5	11,555.7	5,680.7	1,019.0
C1-Dibenz	33,284.0	20,859.0	4,529.7	2,992.5	48,925.1	17,990.5	12,931.0	30,909.5	14,508.6	15,496.6	36,104.0	8,983.0	4,245.3	2,881.0	3,923.3	610.0
C2-Dibenz	16,119.6	12,877.1	3,494.1	2,666.1	23,005.0	11,177.9	9,387.9	22,007.8	8,446.9	9,901.5	24,039.4	6,566.9	3,330.9	2,037.9	3,361.9	663.1
C3-Dibenz	7,628.9	7,215.6	2,344.3	1,840.5	10,709.4	6,194.3	5,726.6	11,521.9	4,682.9	5,584.7	12,112.5	3,980.6	2,246.9	1,353.8	2,245.9	682.1
Fluoranthene	1,309,490.6	886,403.1	260,379.7	181,762.2	1,949,244.6	739,572.9	497,617.9	887,840.3	658,419.4	782,244.2	942,116.0	266,130.4	171,453.6	153,273.1	128,914.1	26,867.5
Pyrene	1,508,524.2	1,038,750.2	305,998.3	214,709.8	2,234,130.6	864,286.8	595,348.6	1,053,428.2	766,514.9	930,829.0	1,113,112.7	319,287.1	208,723.3	178,379.9	160,967.2	31,916.5
C1-Fluor/Pyr	257,386.0	191,321.6	49,511.8	36,216.5	372,702.0	148,578.5	104,310.0	206,242.5	123,899.6	143,596.2	212,878.0	58,660.9	34,514.3	28,906.5	29,330.4	7,442.8
Benz(a)anthracene	431,375.4	322,837.6	91,834.5	67,595.9	724,176.8	269,131.7	177,857.8	309,003.2	238,940.7	282,469.3	331,906.1	96,297.4	54,200.6	52,661.3	46,411.0	12,127.9
Chrysene	430,572.2	315,796.4	95,284.3	73,501.4	700,817.7	271,217.2	188,113.8	321,234.8	268,768.1	323,498.2	341,939.6	109,175.9	62,490.4	54,656.5	53,284.3	12,275.6
C1-Chyrsenes	75,304.2	62,301.3	18,853.4	14,160.0	105,149.4	49,055.6	36,314.7	67,308.4	40,409.8	45,452.7	69,281.0	23,331.2	11,711.4	10,156.8	10,118.9	3,321.2
C2-Chrysenes	18,214.7	16,210.3	4,979.7	4,088.1	25,096.9	12,954.2	10,731.5	17,602.2	10,343.4	12,360.0	17,825.3	6,527.2	3,435.8	2,886.4	2,772.0	1,144.9
C3-Chrysenes	802.7	809.1	412.1	281.9	997.0	637.2	584.4	766.3	519.6	641.8	763.4	360.5	215.5	220.4	161.1	100.7
C4-Chrysenes	12,345.0	9,121.1	2,683.6	2,124.6	22,798.8	7,127.1	5,262.8	7,954.0	6,675.1	8,252.2	8,622.0	2,684.9	1,380.8	1,529.0	1,113.9	380.7
Benzo(b)fluoranthene	557,109.9	451,014.4	149,394.3	112,670.0	935,868.5	360,389.5	243,273.0	397,718.1	330,153.8	395,052.9	420,052.3	138,389.6	75,219.7	77,189.0	59,809.8	17,719.5
Benzo(k)fluoranthene	170,903.2	135,236.8	47,103.6	36,280.7	261,868.3	104,890.5	76,878.2	129,391.3	100,598.9	121,768.5	134,387.4	43,455.6	22,806.2	23,573.7	18,168.9	5,347.8
Benzo(e)pyrene	363,283.9	299,568.7	108,227.9	83,004.8	586,021.1	241,108.9	164,113.8	272,920.7	224,445.7	270,127.6	286,661.9	98,259.6	51,494.9	52,845.1	39,935.1	11,455.6
Benzo(a)pyrene	871,875.4	702,323.6	249,771.9	191,422.4	1,441,908.5	573,396.9	377,951.5	647,953.0	536,655.4	652,372.4	679,564.6	224,829.6	118,816.3	124,851.5	94,606.1	25,451.8
Perylene	154,361.7	129,443.4	44,057.7	34,132.4	267,221.3	107,216.0	75,344.6	114,304.3	96,074.0	117,619.9	125,469.4	40,864.9	21,571.1	22,793.1	16,652.0	4,958.1
Indeno[1,2,3-cd]pyrene	563,211.1	421,732.9	151,112.2	113,889.7	868,548.9	342,460.8	237,604.7	404,569.9	334,639.9	409,365.6	423,338.3	145,403.5	75,026.6	76,374.0	56,721.6	15,262.6
Dibenz(a,h)anthracene	46,830.5	36,001.2	8,063.6	6,085.3	76,171.1	29,094.7	20,340.7	29,834.9	25,475.5	30,088.3	32,551.0	9,462.9	4,651.7	5,293.0	4,025.5	1,681.1
Benzo(ghi)perylene	534,034.8	436,277.2	160,705.0	122,152.2	831,745.9	351,707.9	240,025.4	403,731.0	329,534.2	410,229.5	419,296.4	148,876.2	78,904.0	76,743.9	57,463.6	14,549.1
Total PAHs	**10,077,580.6**	**7,073,131.8**	**2,100,459.2**	**1,495,985.8**	**16,514,849.6**	**5,781,712.3**	**3,822,322.5**	**7,126,899.8**	**5,245,196.8**	**5,985,425.2**	**7,856,020.0**	**2,303,695.2**	**1,281,578.1**	**1,178,019.6**	**926,594.4**	**224,618.5**
Specific Isomers																
2-Methylnaphthalene	17,952.6	16,569.6	5,577.4	4,755.1	56,236.6	16,440.8	11,165.8	24,041.0	9,105.8	7,276.9	38,673.8	10,562.8	3,835.4	2,708.0	2,203.4	786.1
1-Methylnaphthalene	14,283.1	10,476.5	3,276.0	2,376.1	52,457.0	11,376.9	3,239.1	30,599.3	6,609.2	5,382.9	46,921.0	13,965.0	7,214.3	2,161.5	978.8	449.6
2,6-Dimethylnaphthalene	23,375.0	9,742.2	2,962.3	1,687.7	22,106.7	16,136.1	5,646.6	31,282.5	11,066.4	8,198.4	59,435.7	11,190.8	6,226.7	1,502.5	913.6	333.0
1,6,7-Trimethylnaphthalen	12,173.6	6,291.8	1,808.4	847.9	14,435.9	6,729.3	5,665.5	18,590.6	6,063.0	7,357.6	25,756.2	5,647.8	2,526.4	988.3	1,919.8	318.9
1-Methylphenanthrene	41,867.7	25,519.1	5,459.0	3,120.4	56,079.1	22,252.1	16,293.8	42,059.0	18,773.6	21,205.5	49,239.0	11,896.5	5,606.0	4,125.8	5,461.2	759.7

Table A.2. Continued.

Sample Identification	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Sampling Date	3/15/2002	3/15/2002	3/15/2002	3/15/2002	3/15/2002	3/15/2002	3/15/2002	3/15/2002	3/15/2002	7/16/2002	7/16/2002	7/16/2002	7/16/2002	7/16/2002	7/16/2002	7/16/2002
Sampling Location	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Remote Lake	Remote Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake
Naphthalene	1,781.0	1,507.9	2,889.8	2,462.6	1,727.0	1,812.6	1,078.7	54.1	59.2	32,123.0	56,274.9	9,898.8	6,341.1	2,053.3	2,640.9	3,414.2
C1-Naphthalenes	638.6	510.9	865.6	903.6	736.0	570.9	388.4	36.5	50.5	21,842.6	13,251.8	2,493.2	2,108.2	675.7	824.7	1,047.6
C2-Naphthalenes	371.1	306.4	441.0	553.6	516.7	328.3	249.7	30.0	46.6	19,025.0	13,050.7	1,572.6	1,943.3	393.1	435.1	482.7
C3-Naphthalenes	337.9	332.0	425.4	666.1	509.7	305.0	246.8	27.4	51.4	17,399.2	14,009.5	2,757.7	2,852.9	386.8	404.8	467.8
C4-Naphthalenes	237.2	236.4	351.4	822.8	377.0	268.5	218.1	18.1	38.9	7,897.5	7,228.6	3,436.0	1,977.6	326.5	332.3	366.1
Biphenyl	291.6	264.1	474.3	314.1	237.6	274.9	177.6	10.3	16.0	5,573.1	10,316.5	1,311.7	1,013.1	305.3	471.3	596.0
Acenephthylene	623.8	526.1	899.6	668.7	545.2	582.6	380.9	17.4	19.4	9,200.1	15,530.2	2,558.1	2,159.2	723.9	892.0	1,174.4
Acenaphthene	654.0	734.1	913.5	705.6	518.3	556.8	468.6	26.8	67.8	36,422.6	114,993.5	2,259.3	6,021.2	943.3	1,050.4	1,336.3
Fluorene	574.8	612.4	859.2	801.0	572.1	530.6	491.8	27.4	57.2	26,057.8	51,839.4	2,363.8	3,184.7	674.8	836.9	1,101.7
C1-Fluorenes	294.3	292.4	424.9	654.8	354.8	260.7	221.0	15.9	31.3	10,080.0	12,008.5	2,646.9	2,046.2	336.6	419.8	545.3
C2-Fluorenes	410.2	277.0	492.6	897.9	435.4	345.9	336.7	25.0	64.2	8,887.7	10,083.2	3,532.5	2,108.6	418.3	491.5	637.1
C3-Fluorenes	344.8	319.4	582.2	887.1	568.2	460.8	401.7	27.3	90.0	7,956.1	8,271.3	3,678.6	2,098.9	473.1	516.4	630.7
Phenanthrene	2,789.2	3,021.5	4,888.9	2,484.7	2,416.5	2,656.3	2,039.8	109.8	194.1	168,503.8	363,428.6	10,210.6	15,988.3	2,799.5	4,164.4	5,802.3
Anthracene	1,792.1	1,730.8	3,078.7	2,291.9	1,645.5	1,687.5	1,395.1	44.8	84.2	82,155.5	186,843.9	10,691.7	10,949.9	1,818.1	2,542.0	5,250.3
C1-Phen/Anth	1,166.4	1,078.1	1,718.5	1,566.8	1,154.2	1,078.7	879.5	48.0	87.9	37,795.2	56,234.1	7,722.2	5,642.9	1,120.4	1,516.2	2,048.0
C2-Phen/Anth	991.2	855.5	1,324.8	1,857.0	1,067.5	909.3	742.0	44.8	107.3	18,923.1	23,772.5	7,599.8	5,229.6	1,056.0	1,302.9	1,662.3
C3-Phen/Anth	680.6	576.8	834.6	1,327.0	739.6	641.1	537.3	47.2	265.9	8,185.9	9,848.5	4,000.0	2,981.2	720.4	812.0	1,078.3
C4-Phen/Anth	415.4	298.2	401.4	638.8	374.1	328.7	323.3	49.6	510.3	2,620.8	3,031.2	1,488.5	1,013.3	340.3	366.0	466.9
Dibenzothiophene	445.1	469.0	777.1	513.5	360.1	402.4	301.3	11.8	22.4	25,517.2	51,426.1	2,726.9	2,361.6	458.4	686.9	935.3
C1-Dibenz	225.6	194.3	344.9	473.9	248.3	203.9	165.0	8.0	17.5	7,547.9	11,025.8	2,306.9	1,387.4	248.4	321.3	458.2
C2-Dibenz	273.3	196.8	369.5	601.1	317.5	247.2	215.5	9.3	30.6	5,104.0	6,490.6	2,242.5	1,544.2	312.8	357.5	485.5
C3-Dibenz	473.9	410.2	536.6	661.7	450.0	504.1	446.0	16.5	55.3	3,075.0	3,839.6	1,587.2	1,287.4	408.0	483.8	691.4
Fluoranthene	8,740.8	8,272.0	15,873.2	14,148.4	7,946.2	8,525.1	6,304.8	215.4	360.2	291,486.2	513,613.1	82,337.1	50,479.5	9,850.2	14,352.5	22,137.4
Pyrene	10,755.8	10,211.9	18,434.5	16,883.4	9,894.7	10,689.2	7,502.3	234.5	367.5	355,941.8	583,119.9	100,162.9	63,435.7	11,409.4	16,792.7	25,941.9
C1-Fluor/Pyr	2,946.3	2,544.5	4,743.5	4,998.8	2,962.6	2,951.8	2,246.8	71.2	298.9	56,728.6	101,270.3	20,500.1	12,605.0	3,161.5	4,288.6	6,543.3
Benz(a)anthracene	4,683.5	4,369.1	8,493.1	6,942.3	4,145.4	4,401.0	3,370.2	78.5	121.0	98,754.1	192,557.1	32,239.4	17,569.7	5,070.0	7,399.2	11,098.8
Chrysene	4,418.8	3,985.9	7,720.3	5,936.7	4,240.3	4,264.2	3,429.2	97.3	220.8	110,004.3	211,057.3	36,547.0	20,063.9	4,387.6	6,499.0	11,473.0
C1-Chyrsenes	1,562.3	1,358.3	2,315.6	2,149.9	1,561.0	1,540.9	1,301.4	38.5	121.9	19,099.0	33,952.1	7,466.7	5,483.2	1,676.1	2,129.8	3,075.1
C2-Chrysenes	631.7	536.1	828.9	906.8	727.6	591.0	617.4	26.9	108.7	5,472.7	8,633.4	2,090.1	1,782.5	747.2	809.3	1,043.8
C3-Chrysenes	88.2	96.6	95.9	86.5	96.6	91.4	94.2	6.2	21.7	298.8	352.5	157.1	143.1	104.1	115.3	132.9
C4-Chrysenes	189.6	163.5	283.2	211.4	181.5	174.1	142.6	3.0	6.8	2,716.5	5,411.4	793.6	462.1	215.1	298.5	494.0
Benzo(b)fluoranthene	8,103.9	7,379.3	13,267.8	9,517.0	7,384.1	7,600.4	5,754.7	152.7	241.3	137,092.4	266,372.4	41,935.4	24,237.2	8,613.4	13,458.0	20,124.3
Benzo(k)fluoranthene	2,421.9	1,524.0	3,670.5	2,439.4	2,069.9	2,067.8	1,527.7	34.2	56.2	41,459.3	82,931.1	12,781.7	7,925.8	2,610.5	2,630.5	5,637.5
Benzo(e)pyrene	5,373.9	4,374.8	8,244.8	5,892.3	4,838.7	4,818.4	3,518.0	92.2	148.0	92,446.7	178,707.7	28,296.9	16,931.0	5,880.9	8,112.1	13,043.5
Benzo(a)pyrene	11,212.4	9,560.5	18,183.6	12,628.5	9,824.8	10,229.0	7,184.8	166.7	168.6	219,630.0	428,772.7	66,824.9	39,321.3	12,372.5	18,006.8	29,773.1
Perylene	2,746.0	2,341.0	3,977.0	3,067.2	2,462.8	2,437.0	1,856.9	359.5	917.4	39,605.2	74,712.6	12,480.3	7,527.0	2,702.4	3,418.8	4,683.5
Indeno[1,2,3-cd]pyrene	7,087.8	5,973.6	11,135.7	7,707.2	6,501.0	6,588.1	4,615.9	125.3	133.8	133,415.8	260,527.9	40,331.4	23,881.2	7,995.6	11,654.3	19,771.1
Dibenz(a,h)anthracene	803.2	662.2	1,249.3	909.2	776.1	761.4	549.5	11.2	19.4	8,955.4	19,210.1	2,982.4	1,677.2	916.7	1,288.5	2,264.0
Benzo(ghi)perylene	6,614.5	5,745.3	10,275.3	7,185.8	6,199.0	6,344.9	4,404.2	126.0	145.2	136,445.9	260,840.2	41,897.1	25,261.1	7,788.1	11,083.8	18,963.3
Total PAHs	**94,192.5**	**83,848.6**	**152,686.6**	**124,364.7**	**87,683.6**	**89,032.4**	**66,125.2**	**2,544.9**	**5,425.1**	**2,311,445.4**	**4,264,840.5**	**618,909.5**	**401,027.0**	**102,494.3**	**144,206.2**	**226,878.8**
Specific Isomers																
2-Methylnaphthalene	409.4	314.8	561.2	568.8	439.3	370.1	249.5	19.4	28.5	11,362.7	7,103.7	1,728.9	1,180.7	436.5	550.5	681.9
1-Methylnaphthalene	229.2	196.0	304.4	334.8	296.7	200.8	138.9	17.1	22.0	10,479.8	6,148.0	764.3	927.6	239.3	274.3	365.7
2,6-Dimethylnaphthalene	192.4	158.3	243.3	267.5	269.5	170.5	137.1	14.1	19.1	10,686.6	6,196.8	767.7	706.3	209.7	241.2	308.1
1,6,7-Trimethylnaphthalen	100.6	113.6	127.4	204.6	171.5	100.2	77.9	9.4	16.8	4,872.3	3,632.7	1,134.4	955.2	128.9	133.6	163.0
1-Methylphenanthrene	353.3	326.4	506.0	586.8	344.1	293.2	231.6	12.9	32.2	9,707.0	14,373.9	3,154.8	2,118.8	330.0	465.0	627.1

Table A.2. Continued.

Sample Identification	49	50	51	52	53	54	55	56	57	58	59	60	61	62
Sampling Date	7/16/2002	7/16/2002	7/16/2002	7/16/2002	7/16/2002	7/16/2002	8/8/2002	8/8/2002	8/8/2002	8/8/2002	8/8/2002	8/8/2002	8/8/2002	8/8/2002
Sampling Location	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Remote Lake	Remote Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Urban Lake	Remote Lake	Remote Lake
Naphthalene	2,234.0	1,684.9	1,622.0	1,697.2	33.8	116.5	2,313.7	5,243.7	28,233.4	111,834.7	5,808.8	3,785.3	127.7	106.5
C1-Naphthalenes	775.9	599.6	701.4	752.1	17.4	64.9	862.1	1,584.9	7,510.0	24,862.1	1,425.9	1,050.0	40.0	97.9
C2-Naphthalenes	563.2	352.9	348.2	462.4	16.6	61.3	486.0	1,336.1	4,408.8	37,446.7	949.1	799.0	30.3	154.6
C3-Naphthalenes	815.2	357.0	294.5	438.7	25.0	67.7	455.3	2,494.1	4,815.8	39,693.0	1,914.7	1,451.3	31.9	170.6
C4-Naphthalenes	817.1	328.1	241.4	371.5	28.1	53.7	355.3	2,044.6	2,753.2	18,382.1	2,242.8	1,323.1	23.3	92.2
Biphenyl	302.7	266.7	251.4	297.3	7.3	21.2	350.5	837.9	5,426.7	22,512.9	819.8	574.4	17.8	26.2
Acenephthylene	738.8	583.4	516.0	654.7	7.9	43.8	867.1	1,444.5	11,502.6	28,341.7	1,670.9	1,008.2	24.7	52.2
Acenaphthene	876.7	643.8	582.8	858.0	18.9	46.8	568.2	4,622.9	36,856.8	287,381.9	1,825.8	2,019.4	24.9	245.8
Fluorene	783.2	501.5	535.4	767.2	17.9	60.6	630.9	2,641.9	17,462.4	155,196.3	1,524.6	1,264.6	33.0	292.6
C1-Fluorenes	575.6	293.0	230.8	358.1	10.5	50.6	389.3	1,981.4	5,130.6	34,383.1	1,507.2	1,152.4	18.8	182.1
C2-Fluorenes	816.8	417.0	295.0	576.1	18.9	103.0	505.7	2,139.7	4,225.6	24,790.2	2,388.9	1,450.9	36.2	177.7
C3-Fluorenes	882.3	508.4	353.1	675.0	18.9	117.6	491.8	2,083.6	4,712.6	19,354.1	2,531.7	1,692.9	36.3	143.4
Phenanthrene	3,408.8	2,176.6	2,820.7	3,176.0	71.3	276.0	2,918.6	15,212.4	49,039.9	1,303,360.7	9,097.1	5,636.0	174.4	1,708.3
Anthracene	3,039.9	1,532.1	1,696.7	2,039.4	24.3	169.8	2,218.2	9,767.9	26,912.9	578,424.2	8,137.0	5,444.8	71.2	795.2
C1-Phen/Anth	2,004.6	941.9	1,101.1	1,448.5	30.4	155.9	1,327.1	5,615.3	17,869.7	160,612.5	5,704.1	3,661.9	62.2	749.3
C2-Phen/Anth	1,979.3	939.7	897.8	1,260.8	30.1	148.5	1,249.4	4,163.4	12,211.8	52,167.7	5,110.9	3,154.7	54.1	399.4
C3-Phen/Anth	1,604.1	759.8	615.4	896.9	28.8	194.9	815.2	2,573.7	5,538.0	20,997.7	3,010.2	2,067.5	53.6	-
C4-Phen/Anth	755.5	381.9	312.0	426.5	31.9	277.5	328.8	985.8	2,150.0	14,166.1	1,308.9	945.8	45.6	-
Dibenzothiophene	612.8	355.7	406.8	471.2	7.6	28.0	495.4	2,284.0	16,830.5	187,815.7	1,597.6	1,133.0	19.3	69.7
C1-Dibenz	534.4	221.2	207.3	284.0	6.0	23.0	287.4	1,461.9	4,268.0	30,624.5	1,446.3	1,039.3	11.0	59.6
C2-Dibenz	658.4	289.1	254.1	368.4	6.1	40.6	335.7	1,292.9	3,268.1	14,227.8	1,445.9	966.1	13.4	73.8
C3-Dibenz	735.8	424.2	442.5	686.3	7.0	64.1	437.6	1,050.0	2,444.1	6,763.8	1,298.1	935.0	16.7	167.3
Fluoranthene	15,260.8	9,525.4	9,189.8	10,982.9	97.9	522.6	10,456.0	44,202.6	234,760.6	1,312,182.1	52,731.7	32,299.3	374.4	2,150.7
Pyrene	18,430.8	11,191.0	10,385.5	12,450.2	91.5	548.6	12,003.4	54,100.3	279,298.0	1,574,137.3	65,195.1	39,439.5	440.8	1,948.0
C1-Fluor/Pyr	5,208.4	2,995.4	2,838.1	3,553.8	36.1	277.5	3,596.2	10,414.5	46,859.1	230,864.1	12,882.6	7,393.7	121.0	1,925.6
Benz(a)anthracene	6,963.7	4,754.3	4,483.8	5,293.9	28.0	192.6	5,512.8	14,867.4	80,828.3	440,932.8	19,273.0	10,684.7	165.3	742.8
Chrysene	7,348.4	4,446.5	3,901.7	5,400.3	35.8	327.8	5,549.0	17,181.9	80,567.4	467,313.0	23,341.9	12,764.8	178.9	778.1
C1-Chyrsenes	2,571.7	1,700.6	1,469.4	1,899.7	16.9	162.8	2,046.1	4,023.2	17,647.4	66,182.8	4,903.4	3,122.2	63.2	331.1
C2-Chrysenes	1,041.0	748.1	671.6	827.1	13.5	126.0	934.7	1,428.0	5,138.3	15,688.8	1,705.7	1,180.7	42.6	143.7
C3-Chrysenes	99.7	104.1	103.5	110.8	3.9	31.5	105.4	99.9	293.9	785.2	122.4	123.7	9.8	28.4
C4-Chrysenes	251.9	198.3	185.1	204.0	1.2	12.7	294.8	461.4	2,382.5	11,204.9	511.1	371.9	6.5	13.6
Benzo(b)fluoranthene	10,412.3	8,607.4	7,523.1	9,172.8	44.5	414.6	11,748.5	20,275.6	127,049.8	550,118.7	25,857.3	14,237.7	283.2	910.1
Benzo(k)fluoranthene	3,027.0	2,100.4	2,193.9	2,083.1	13.7	96.3	2,476.8	6,263.3	37,648.2	178,015.8	8,609.5	4,601.6	70.4	252.1
Benzo(e)pyrene	6,733.2	5,345.1	4,934.6	5,435.8	28.0	245.5	7,935.5	14,026.5	88,541.6	366,722.6	17,657.7	10,022.1	175.9	475.4
Benzo(a)pyrene	14,824.3	11,318.7	10,508.1	11,650.1	45.0	333.9	16,387.5	31,867.4	202,162.5	891,619.9	41,735.1	22,509.0	351.5	1,018.7
Perylene	2,911.4	2,446.5	2,276.5	2,484.0	263.3	1,158.5	3,237.7	6,239.1	36,573.9	158,039.1	8,155.4	4,373.5	357.4	1,132.3
Indeno[1,2,3-cd]pyrene	8,970.5	7,352.4	6,698.6	7,333.6	36.7	251.2	11,219.8	19,166.0	129,681.6	538,668.6	24,575.0	13,276.0	234.2	551.0
Dibenz(a,h)anthracene	1,051.4	858.3	772.0	856.0	3.5	37.2	1,273.3	1,324.2	7,851.3	40,175.2	1,790.6	968.8	22.4	80.2
Benzo(ghi)perylene	8,612.4	6,989.8	6,510.3	7,099.0	38.2	256.4	10,687.1	20,484.8	134,820.8	530,735.2	25,362.2	14,036.7	229.2	508.1
Total PAHs	**139,233.7**	**95,240.6**	**89,371.8**	**105,803.2**	**1,262.2**	**7,181.7**	**124,153.6**	**339,288.6**	**1,785,676.5**	**10,546,725.1**	**397,175.8**	**233,961.2**	**4,093.1**	**18,754.0**
Specific Isomers														
2-Methylnaphthalene	497.3	394.1	466.2	467.1	9.9	41.3	535.5	991.7	4,497.9	14,860.4	986.0	715.6	26.0	50.6
1-Methylnaphthalene	278.7	205.5	235.2	285.0	7.4	23.6	326.6	593.2	3,012.0	10,001.8	440.0	334.4	14.0	47.4
2,6-Dimethylnaphthalene	255.7	186.3	179.5	254.6	5.5	26.9	278.4	547.2	1,982.3	16,628.2	454.3	334.5	13.2	58.6
1,6,7-Trimethylnaphthalen	245.9	116.8	89.3	145.4	9.9	20.8	163.6	851.3	1,374.3	10,794.0	662.1	531.8	9.9	53.6
1-Methylphenanthrene	685.8	296.1	307.0	428.1	8.9	48.5	423.1	1,903.5	5,387.2	37,339.6	2,127.1	1,349.5	17.5	236.1

Table A.3.
Stable carbon isotope ratios (‰) of PAHs in sediment samples for Chapter V.

	Sample Identification	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**Naphthalene**	-23.26	-25.54	-24.62	-24.32	-24.27	-23.95	-24.69	-23.40	-23.48	-24.09	-23.64	-23.55	-23.02	-24.08	-22.83	-22.33	-22.73	-23.18
2	**2-Methylnaphthalene**	-19.94	-15.37	-22.12	-18.86	-19.14	-22.76	-16.17	-21.79	-21.76	-21.81	-21.46	-19.12	-21.91		-21.43	-21.01		
3	**1-Methylnaphthalene**	-27.25		-23.49	-25.45	-22.70	-23.02	-27.88	-22.72	-21.34	-22.50	-19.84	-25.43	-16.37		-22.27	-21.78		
4	**2+3**	-19.40	-13.54	-21.42	-23.90	-23.54	-25.11	-14.93	-22.36	-21.19	-22.15	-22.16	-21.69	-22.32		-23.10	-20.11	-19.08	-20.45
5	**Biphenyl**	-22.79	-13.62	-20.68	-16.95	-25.67	-15.45	-17.59	-22.66	-23.44	-22.26	-22.22	-21.70	-21.82	-22.58	-20.41	-21.50	-20.76	-21.32
6	**2,6-Dimethylnaphthalene**	-35.44	-20.19	-22.04	-17.11	-21.80	-26.65		-21.72	-19.82	-19.87	-21.22	-15.94	-17.61		-16.72	-17.35	-20.18	
7	**Acenaphthylene**	-25.20	-28.97	-25.65	-21.93	-25.97	-27.49	-18.79	-23.04	-23.96	-20.55	-23.58	-21.60	-21.25	-23.69	-22.91	-22.15	-33.84	
8	**Acenaphthene**	-21.88	-23.09	-23.00	-23.21	-20.71	-20.69	-18.01	-22.51	-22.15	-22.40	-23.66	-23.37	-23.40	-25.23	-22.37	-21.97	-22.35	-23.38
9	**1,6,7-Trimethylnaphthalene**		-27.53	-28.92	-18.15					-21.11				-17.99					
10	**Fluorene**	-23.46	-20.95	-23.55	-23.33	-19.25	-24.40	-23.40	-22.32	-21.94	-23.66	-22.90	-23.73	-22.00	-23.07	-21.55	-21.77	-21.44	-23.90
	Dibenzothiophene	-24.33	-33.96		-23.01	-24.11	-21.54	-21.23	-23.35	-22.30	-23.10	-22.83	-21.88	-22.30	-22.24	-23.01	-22.40	-22.48	-23.86
11	**Phenanthrene**	-23.45	-23.48	-23.31	-22.82	-22.85	-22.75	-23.20	-22.78	-22.87	-23.14	-23.18	-22.44	-22.14	-22.44	-22.27	-22.44	-22.38	-22.59
12	**Anthracene**	-23.76	-24.00	-23.70	-23.24	-23.67	-23.36	-24.16	-24.27	-24.53	-24.42	-24.89	-23.93	-24.70	-24.89	-23.83	-24.32	-24.51	-24.02
13	**11+12**	-23.42	-23.18	-23.54	-23.03	-23.11	-23.05	-23.34	-23.16	-23.13	-23.49	-23.40	-22.73	-22.71	-22.83	-22.55	-22.80	-22.80	-22.97
14	**1-Methylphenanthrene**	-23.49	-23.45	-23.49	-22.15	-21.25	-23.89	-22.83	-23.04	-22.84	-23.10	-22.43	-23.02	-22.68	-22.24	-21.99	-21.75	-21.56	-21.20
	C1-Phenanthrenes/Anthracen	-23.11	-24.13	-23.03	-22.77	-22.36	-23.24	-23.44	-22.92	-22.84	-22.88	-23.11	-22.82	-22.81	-22.51	-22.91	-22.22	-22.92	-22.39
15	**Fluoranthene**	-24.22	-24.46	-23.77	-23.68	-23.36	-23.37	-24.56	-23.16	-23.22	-23.72	-23.76	-23.76	-24.05	-23.21	-23.60	-23.43	-23.53	-23.63
16	**Pyrene**	-24.09	-24.32	-23.70	-23.37	-23.21	-23.52	-24.18	-23.18	-23.37	-23.70	-23.72	-23.80	-23.89	-23.34	-23.61	-24.13	-23.38	-23.44
19	**17+18**	-23.53	-23.22	-23.47	-23.31	-22.56	-22.45	-23.20	-22.98	-23.37	-23.68	-23.10	-23.28	-23.24	-22.71	-22.73	-22.76	-22.49	-23.04
22	**20+21**	-23.63	-23.59	-23.40	-23.57	-23.02	-23.19	-24.02	-23.60	-23.79	-23.76	-23.45	-22.92	-23.19	-22.84	-23.40	-22.78	-22.80	-23.43
23	**Benzo[e]pyrene**	-23.60	-23.42	-22.46	-22.71	-22.56	-23.62	-23.70		-23.47	-24.62	-24.38	-22.89	-24.03	-22.48	-23.77	-23.41	-22.52	-23.72
24	**Benzo[a]pyrene**	-24.22	-24.69	-23.96	-23.76	-24.24	-24.33	-24.87		-23.81	-24.83	-24.48	-24.10	-24.34	-23.72	-24.20	-23.92	-23.08	-24.41
25	**Perylene**	-23.56	-24.46	-23.81	-24.66	-24.26	-27.41	-25.64		-24.36	-26.79	-25.45	-25.04	-23.08	-24.81	-26.10	-20.24	-24.67	-27.99
26	**23+24+25**	-23.33	-23.98	-23.67	-23.47	-24.01	-23.89	-25.53	-23.62	-23.92	-23.93	-24.03	-24.02	-23.45	-23.78	-23.69	-23.06	-23.24	-23.50
29	**27+28**	-23.09	-23.24	-23.00	-25.78	-22.92	-21.82	-23.32	-23.16	-23.77	-23.45	-23.30	-22.84	-23.38	-23.05	-22.86	-23.04	-22.93	-22.93
30	**Benzo[ghi]perylene**	-22.82	-23.68	-23.59	-25.53	-22.77	-21.46	-23.92	-23.15	-23.76	-23.58	-23.91	-22.80	-23.30	-23.40	-23.21	-23.26	-23.41	-23.50

Table A.3.
Continued.

	Sample Identification	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
1	**Naphthalene**	-23.05	-23.24	-21.70	-26.67	-23.17	-23.80	-23.42	-23.53	-24.11	-22.89	-24.32	-24.02	-24.34	-24.45	-23.30	-24.84	-23.49	-23.22
2	**2-Methylnaphthalene**	-23.74	-20.10	-19.46	-20.17		-19.90												
3	**1-Methylnaphthalene**	-21.23	-24.20	-20.61			-21.85				-20.34								
4	**2+3**	-22.01	-24.55	-20.48	-14.15	-20.18	-20.74	-17.07	-17.83	-21.33	-20.49	-19.55				-22.20	-19.12	-24.31	-24.25
5	**Biphenyl**	-21.18	-22.12	-20.50	-21.41	-21.51	-21.85	-17.73	-20.12							-21.16	-19.53		-20.35
6	**2,6-Dimethylnaphthalene**	-17.58	-13.20			-15.64	-18.37	-14.85		-18.73	-20.19					-11.99	-16.42		-17.77
7	**Acenaphthylene**	-21.48	-23.00	-20.85		-18.17	-19.76	-15.13	-18.21	-18.93	-17.49	-13.72			-12.56	-18.69	-20.25	-20.22	-17.85
8	**Acenaphthene**	-23.15	-23.21	-22.02	-22.46	-22.59	-22.09	-21.94	-22.03	-22.34	-21.89	-21.59	-22.32	-25.08	-22.35	-20.52	-21.70	-20.91	-21.16
9	**1,6,7-Trimethylnaphthalene**						-15.50			-15.79	-13.57								
10	**Fluorene**	-22.05	-23.08	-21.76	-22.31	-21.97	-22.92	-20.05	-20.42	-22.50	-22.45	-21.64	-20.31	-21.08	-20.11	-22.22	-20.56	-19.92	-21.40
	Dibenzothiophene	-22.26	-22.27	-21.64	-22.21	-22.28	-21.88	-21.99	-22.39	-21.93	-21.94	-21.54	-22.12	-22.45	-20.40	-21.00	-21.69	-21.62	-21.03
11	**Phenanthrene**	-22.04	-21.85	-22.17	-22.84	-22.75	-23.23	-22.84	-22.21	-23.34	-22.54	-21.56	-22.58	-22.14	-22.07	-22.15	-22.20	-22.46	-22.47
12	**Anthracene**	-25.93		-24.05	-24.66	-24.14	-24.12	-24.82	-24.18	-24.65	-24.27	-25.27	-24.80	-24.13	-23.81	-24.47	-24.46	-24.23	-23.52
13	**11+12**	-22.67	-22.86	-22.54	-23.18	-23.14	-23.42	-23.30	-23.08	-23.62	-22.97	-22.66	-23.30	-22.80	-22.64	-22.78	-22.78	-23.37	-23.15
14	**1-Methylphenanthrene**	-21.15	-21.63	-21.62	-21.79	-21.11	-21.78	-21.75	-21.23	-21.48	-21.31	-20.87	-21.40	-21.96	-20.07	-22.67	-21.64	-21.60	-21.51
	C1-Phenanthrenes/Anthracen	-22.64	-22.66	-22.81	-22.49	-22.97	-22.86	-23.03	-22.64	-22.61	-22.67	-22.33	-22.72	-22.32	-23.31	-22.38	-22.84	-18.65	-22.54
15	**Fluoranthene**	-23.66	-23.66	-23.38	-23.68	-23.96	-23.82	-23.69	-23.89	-23.88	-23.54	-23.56	-23.85	-23.63	-23.06	-23.80	-23.59	-23.90	-23.70
16	**Pyrene**	-23.52	-23.52	-23.32	-23.58	-23.82	-23.83	-23.79	-23.72	-23.96	-23.44	-23.53	-23.65	-23.77	-23.34	-23.26	-23.64	-23.80	-23.71
19	**17+18**	-22.66	-23.01	-22.63	-22.97	-23.23	-23.06	-22.74	-23.17	-23.50	-22.85	-22.92	-23.05	-23.19	-22.63	-22.68	-23.44	-23.28	-22.94
22	**20+21**	-23.67	-23.45	-22.92	-23.16	-23.51	-23.24	-23.41	-23.45	-23.06	-22.85	-23.10	-23.27	-23.19	-23.18	-23.50	-23.31	-23.19	-23.33
23	**Benzo[e]pyrene**	-23.70	-23.60	-23.77	-24.35	-23.35	-24.29	-23.73	-23.47	-25.18	-23.81	-22.89	-24.22	-23.71	-23.60	-23.80	-24.17	-24.31	-24.23
24	**Benzo[a]pyrene**	-24.15	-23.81	-23.94	-24.35	-23.86	-24.32	-23.91	-23.94	-24.30	-24.14	-23.52	-24.46	-24.51	-23.84	-24.41	-24.73	-24.47	-24.52
25	**Perylene**	-25.56	-24.90	-26.37	-23.50	-24.66	-26.09	-20.88	-25.53	-25.36	-24.92	-24.32	-19.59	-25.11	-23.46	-24.86	-24.32	-26.48	-26.48
26	**23+24+25**	-23.57	-23.99	-23.14	-23.64	-23.85	-23.78	-23.61	-24.18	-23.68	-23.88	-23.52	-23.90	-23.64	-23.11	-24.04	-24.13	-23.73	-24.70
29	**27+28**	-23.37	-23.22	-22.75	-23.05	-23.96	-23.13	-23.56	-23.29	-23.87	-23.26	-23.34	-24.11	-23.42	-22.51	-23.36	-23.33	-23.00	-23.41
30	**Benzo[ghi]perylene**	-23.71	-23.53	-23.12	-23.17	-23.89	-23.82	-23.13	-24.01	-23.76	-23.72	-24.12	-23.80	-23.75	-23.37	-23.03	-22.89	-21.72	-23.45

Table A.3.
Continued.

	Sample Identification	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
1	**Naphthalene**	-25.19	-25.16									-24.76	-23.92	-21.89	-23.25	-21.70			-35.26
2	**2-Methylnaphthalene**																		
3	**1-Methylnaphthalene**																		
4	**2+3**		-20.35	-16.05			-18.94	-25.74	-25.48	-41.67	-20.48	-21.15	-22.13	-21.14	-19.63	-18.57			
5	**Biphenyl**		-19.27													-21.50			
6	**2,6-Dimethylnaphthalene**		-18.68				-17.00					-17.88		-17.45		-16.14			
7	**Acenaphthylene**	-22.57	-20.88	-21.65			-20.24			-19.24	-18.41	-19.67		-22.93	-16.95	-19.16			-10.51
8	**Acenaphthene**	-20.58	-21.45	-22.88	-36.53		-22.19	-22.55	-20.88	-21.39	-21.69	-21.90	-18.73	-22.07	-22.39	-20.73		-42.72	-26.74
9	**1,6,7-Trimethylnaphthalene**		-23.23	-29.92			-19.33			-5.95		-18.71		-23.72		-25.07			
10	**Fluorene**	-19.57	-20.77	-23.16	-22.27		-21.85	-20.76	-20.89	-20.98	-21.81	-20.31	-21.95	-20.16	-21.62	-22.97		-14.93	-26.17
	Dibenzothiophene	-20.84	-20.48	-21.07	-22.53		-22.45		-21.67	-21.44	-20.74	-22.27	-21.87	-22.22	-21.66	-19.39			
11	**Phenanthrene**	-23.08	-23.29	-21.60	-23.99		-22.52	-23.84	-21.75	-22.29	-22.65	-23.34	-21.98	-21.50	-21.62	-21.50	-20.33	-25.60	-21.94
12	**Anthracene**	-24.87	-25.47				-24.28	-25.26	-24.65	-24.97	-25.97	-25.38	-25.99	-24.72	-25.54	-25.96	-25.27		
13	**11+12**	-23.59	-23.77	-22.78	-23.94		-23.48	-23.27	-23.10	-23.25	-23.84	-23.97	-22.47	-22.35	-23.00	-22.99	-22.13	-26.63	-22.51
14	**1-Methylphenanthrene**	-21.09	-21.85	-21.54	-24.80		-20.66	-21.00	-20.99	-20.93	-21.88	-20.62	-21.21	-20.38	-21.26	-20.48	-20.91	-24.53	-23.95
	C1-Phenanthrenes/Anthracen	-22.87	-22.65	-22.67	-27.86		-22.93	-22.77	-21.94	-22.36	-22.96	-22.26	-22.07	-21.65	-21.58	-21.77		-30.09	-24.46
15	**Fluoranthene**	-23.69	-24.24	-24.07	-27.47	-24.89	-23.48	-23.91	-23.63	-23.79	-23.94	-22.90	-23.26	-23.27	-23.91	-23.80	-23.71	-23.02	-24.67
16	**Pyrene**	-23.65	-23.77	-23.74	-25.35	-24.77	-23.67	-23.88	-23.62	-23.26	-23.50	-23.03	-23.76	-23.47	-23.69	-23.73	-23.21	-23.27	-24.53
19	**17+18**	-23.50	-23.05	-23.18	-26.43	-25.06	-22.97	-23.17	-23.12	-22.72	-23.14	-23.03	-22.73	-23.16	-22.71	-23.40	-22.17	-25.25	-23.88
22	**20+21**	-23.81	-23.37	-23.29	-26.34		-23.02	-23.29	-23.10	-22.74	-23.82	-23.34	-22.94	-23.46	-23.25	-23.30	-23.20	-23.91	-23.40
23	**Benzo[e]pyrene**	-23.74	-24.70	-24.52			-24.02	-24.07	-23.70	-22.24		-23.47	-23.39	-24.19	-22.61	-23.42	-22.49	-28.08	-25.51
24	**Benzo[a]pyrene**	-23.66	-24.99	-24.68			-24.21	-24.37	-24.19	-22.85		-23.94	-23.91	-24.61	-23.52	-23.94	-23.63	-24.69	-25.59
25	**Perylene**	-24.83	-20.99	-27.77	-29.43		-25.40	-26.74	-22.55	-24.49		-24.69	-25.25	-25.32	-24.87	-24.28	-25.38	-31.47	-28.90
26	**23+24+25**	-23.95	-24.17	-24.27	-25.92		-23.23	-23.70	-23.22	-23.13	-23.61	-23.94	-23.24	-23.64	-23.69	-23.99	-23.99	-30.09	-27.97
29	**27+28**	-23.40	-23.05	-23.16	-26.37	-27.66	-23.80	-22.92	-23.62	-22.55	-23.60	-23.34	-23.02	-22.96	-23.18	-23.38	-22.21		-30.76
30	**Benzo[ghi]perylene**	-24.14	-23.97	-23.41	-28.27		-23.38	-23.54	-23.45	-23.40	-23.33	-23.65	-23.72	-23.30	-23.70	-23.91	-22.88	-26.88	-28.89

Table A.3.
Continued.

	Sample Identification	55	56	57	58	59	60	61	62
1	Naphthalene	-21.66	-23.51	-22.67	-22.76	-37.10	-22.09		-24.56
2	2-Methylnaphthalene								
3	1-Methylnaphthalene								
4	2+3	-19.32	-3.95	-18.83					-19.87
5	Biphenyl								
6	2,6-Dimethylnaphthalene	-24.49							-37.85
7	Acenaphthylene	-16.86		-16.31		-14.31			-14.86
8	Acenaphthene	-19.44	-21.17	-21.08	-22.36		-21.45		-22.15
9	1,6,7-Trimethylnaphthalene		-21.72						-27.90
10	Fluorene	-19.55	-26.34	-20.68	-21.28	-14.22			-25.26
	Dibenzothiophene	-20.40	-22.04	-22.40	-22.45	-25.01			-17.33
11	Phenanthrene	-20.46	-21.77	-20.99	-23.36	-20.81	-20.99	-23.26	-21.96
12	Anthracene	-25.22	-25.68	-26.24	-26.88	-25.49	-24.16		
13	11+12	-22.21	-22.72	-21.86	-23.97	-22.90	-22.12	-23.84	-22.80
14	1-Methylphenanthrene	-20.93	-21.14	-21.54	-22.11	-22.10	-20.84	-30.58	-23.03
	C1-Phenanthrenes/Anthracen	-22.16	-22.39	-21.81	-22.50	-21.78			-24.69
15	Fluoranthene	-23.33	-23.35	-23.87	-23.57	-23.56	-23.73	-26.02	-23.14
16	Pyrene	-23.65	-22.91	-23.48	-23.07	-23.80	-23.41	-24.29	-23.62
19	17+18	-23.99	-22.42	-22.52	-23.26	-23.31	-23.35	-23.95	-25.00
22	20+21	-23.22	-23.58	-23.23	-23.29	-23.05	-23.83	-24.43	-24.35
23	Benzo[e]pyrene	-22.32	-21.53	-23.35	-23.60	-23.36	-23.28	-23.20	-23.67
24	Benzo[a]pyrene	-23.51	-22.94	-23.80	-24.13	-23.82	-23.67	-24.05	-23.75
25	Perylene	-24.95	-24.08	-25.24	-25.75	-25.05	-25.90	-28.26	-27.50
26	23+24+25	-23.65	-23.58	-23.92	-23.89	-23.39	-23.78	-25.54	-25.26
29	27+28	-23.68	-23.03	-22.59	-23.20	-24.44	-23.20	-21.16	-26.90
30	Benzo[ghi]perylene	-23.46	-23.48	-23.62	-23.66	-23.63	-23.23	-25.25	-26.79

Table A.4.
Concentrations (ng/g) of PAHs in marine sediment samples for Chapter VI.

Station Year	A1 2000	A2 2000	A3 2000	B1 2000	B2 2000	B3 2000	C 2000	A 2001	B 2001	C1 2001	C2 2001
Total PAH	**1473.73**	**1077.37**	**1324.11**	**1261.73**	**1764.48**	**2052.62**	**1519.87**	**1410.82**	**5023.97**	**621.11**	**2230.92**
Naphthalene	52.67	45.54	25.88	101.66	59.65	57.12	107.85	18.59	353.03	53.12	8.74
C1-Naphthalenes	183.81	100.51	82.45	241.51	169.37	164.87	281.09	49.07	939.40	108.26	16.53
C2-Naphthalenes	151.33	79.34	180.94	151.52	131.39	112.01	227.16	126.34	857.78	63.91	11.83
C3-Naphthalenes	191.54	46.53	233.23	77.55	74.79	56.19	116.67	306.18	450.55	24.43	6.13
C4-Naphthalenes	154.05	32.62	140.62	41.34	50.55	27.10	54.81	240.50	248.85	7.55	2.83
Biphenyl	33.23	39.43	15.92	26.09	26.43	40.74	38.73	13.59	78.03	13.80	2.50
Acenaphthylene	6.07	4.91	4.47	8.45	7.38	9.62	8.20	14.05	17.57	2.01	4.55
Acenaphthene	7.18	15.77	9.31	7.93	13.01	4.29	9.47	6.31	24.15	1.17	1.99
Fluorene	8.26	22.33	12.31	16.38	16.89	13.12	17.98	3.83	39.88	3.14	4.27
C1-Fluorenes	18.83	11.78	18.40	14.85	18.79	19.55	19.81	25.67	40.24	3.45	2.65
C2-Fluorenes	37.03	14.21	28.13	21.12	33.73	30.39	30.10	48.05	60.20	4.66	5.28
C3-Fluorenes	36.73	18.41	34.36	27.98	36.10	40.45	32.00	44.09	83.85	4.59	5.26
Phenanthrene	26.25	44.59	35.78	44.34	65.36	50.43	49.28	17.33	105.51	17.28	14.64
Anthracene	17.11	19.15	14.66	19.61	26.50	24.40	23.13	8.90	38.10	6.47	30.09
C1-Phenanthrenes/Anthracenes	21.40	21.05	23.26	25.15	53.66	48.72	27.55	24.76	70.43	11.64	32.12
C2-Phenanthrenes/Anthracenes	37.57	23.46	37.95	32.61	71.81	47.40	33.73	48.72	114.27	11.46	39.81
C3-Phenanthrenes/Anthracenes	40.34	24.03	39.61	42.89	77.41	68.43	35.55	47.17	145.55	11.88	55.81
C4-Phenanthrenes/Anthracenes	22.58	12.58	18.64	19.91	42.08	54.46	19.68	25.74	78.80	5.05	43.09
Dibenzothiophene	4.38	4.29	5.19	7.62	8.21	7.82	7.49	5.88	25.87	2.58	2.62
C1-Dibenzothiophenes	11.20	6.98	11.98	13.24	21.33	19.12	16.04	18.86	53.92	4.51	4.07
C2-Dibenzothiophenes	30.82	17.87	30.98	28.13	54.11	40.88	33.16	42.79	137.24	6.65	8.55
C3-Dibenzothiophenes	47.43	26.59	39.92	38.75	67.30	82.35	40.20	67.05	240.66	7.87	12.65
Fluoranthene	42.18	67.76	53.30	39.56	86.05	84.57	43.20	28.76	120.06	31.75	241.09
Pyrene	48.64	62.24	47.29	39.36	83.40	88.54	43.01	32.67	118.83	29.62	219.18
C1-Fluoranthenes/Pyrenes	29.95	30.11	23.45	21.89	58.34	61.30	23.24	21.38	77.60	17.45	127.54
Benzo(a)anthracene	18.03	28.78	17.01	13.06	32.12	53.59	14.05	11.10	55.82	17.74	165.07
Chrysene	28.52	36.27	23.38	17.43	131.12	86.75	22.38	18.50	64.13	19.60	125.08
C1-Chrysenes	23.71	22.97	15.03	16.60	36.62	90.28	18.17	15.83	62.95	13.45	93.91
C2-Chrysenes	20.70	21.17	12.36	18.22	27.13	119.76	19.80	12.82	69.83	13.20	59.47
C3-Chrysenes	3.00	2.71	1.72	3.34	2.84	23.39	2.65	1.81	7.39	2.86	7.39
C4-Chrysenes	1.04	2.52	1.16	1.83	2.72	21.30	1.72	0.00	2.90	0.69	1.43
Benzo(b)fluoranthene	30.77	42.69	23.07	18.82	45.57	82.88	24.95	15.47	53.32	20.37	200.47
Benzo(k)fluoranthene	9.58	14.59	8.13	5.35	10.79	20.82	7.21	6.19	22.15	9.39	76.30
Benzo(e)pyrene	17.97	23.68	11.60	12.84	26.08	79.91	15.95	10.18	36.29	14.43	95.99
Benzo(a)pyrene	19.63	34.16	15.32	14.59	32.92	71.37	15.98	9.15	47.25	21.54	215.43
Perylene	6.36	8.24	4.12	3.35	7.54	12.39	4.64	5.60	24.91	6.47	43.39
Indeno(1,2,3-cd)pyrene	15.05	21.85	10.74	11.50	25.06	47.16	14.23	7.13	23.16	11.79	125.38
Dibenzo(a,h)anthracene	3.39	4.98	2.48	2.44	5.88	20.06	2.87	1.62	5.76	2.46	22.46
Benzo(ghi)perylene	15.43	20.67	9.96	13.04	24.53	69.20	16.14	9.13	27.73	12.82	95.41
2-Methylnaphthalene	107.51	72.34	64.08	168.63	119.75	116.88	194.09	35.53	646.11	82.52	11.79
1-Methylnaphthalene	76.30	28.17	18.37	72.89	49.63	47.99	87.00	13.54	293.29	25.74	4.74
2,6-Dimethylnaphthalene	74.15	46.45	75.14	62.61	69.75	64.20	109.35	69.55	303.82	36.69	7.33
1,6,7-Trimethylnaphthalene	36.99	11.63	38.51	15.33	16.52	14.00	24.96	62.30	60.44	4.93	1.74
1-Methylphenanthrene	7.96	7.28	8.51	9.10	17.85	14.97	8.71	8.98	27.24	3.38	9.64

Table A.5.
Concentrations (ng/g) of PAHs in soil samples for Chapter VI.

Sample Identification	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10	Soil 11	Soil 12
	FS*	OT*	MS*	HP*	FS*	OT*	HP*	MS*	OT*	FS*		HP*
Year	1999	1999	1999	1999	2000	2000	2000	2000	2001	2001	2001	2001
Total PAH	**18,746.0**	**46,479.0**	**1,724.2**	**3,319.8**	**74,267.4**	**28,703.7**	**21,479.5**	**3,806.9**	**56,645.4**	**46,350.8**	**6,757.8**	**9,690.3**
Naphthalene	122.9	932.8	11.5	83.5	1492.2	245.8	404.4	22.6	1104.9	1427.6	369.5	106.0
C1-Naphthalenes	2687.7	11050.2	87.1	327.5	18136.2	4464.6	5536.9	250.8	9778.2	9958.3	2358.4	2056.3
C2-Naphthalenes	4079.5	15602.7	110.9	974.7	27587.2	11581.7	7920.1	336.8	20984.4	23076.3	1197.9	3373.6
C3-Naphthalenes	2901.3	9234.4	119.2	1153.4	13894.6	7184.9	3621.5	213.1	14735.6	6562.3	538.8	1794.1
C4-Naphthalenes	1063.7	2647.7	78.9	318.0	3709.7	1936.4	856.3	131.5	3817.8	1141.3	142.5	459.4
Biphenyl	39.8	799.1	3.2	25.1	1500.3	212.7	752.5	10.8	1495.9	1160.6	16.5	44.6
Acenaphthylene	49.6	202.4	2.9	17.1	299.9	163.2	104.8	5.7	255.0	237.1	10.3	21.7
Acenaphthene	187.4	527.9	12.0	90.3	657.8	462.6	318.4	16.6	619.0	624.4	18.4	21.4
Fluorene	337.8	631.9	9.7	35.2	859.1	438.7	201.7	17.1	429.0	364.1	21.9	95.1
C1-Fluorenes	974.3	823.5	28.6	51.5	1025.2	519.1	176.9	73.0	897.5	303.1	44.0	208.3
C2-Fluorenes	1228.2	884.1	84.1	41.5	880.1	347.2	266.2	196.4	549.3	304.9	116.8	284.3
C3-Fluorenes	894.2	876.5	344.8	44.2	632.8	287.7	296.5	339.1	320.5	264.0	255.7	434.4
Phenanthrene	465.2	287.1	14.6	4.3	402.6	137.4	104.8	40.2	271.4	130.5	21.8	31.0
Anthracene	189.7	33.0	9.3	2.7	43.0	17.0	7.9	7.9	30.2	21.6	5.2	9.7
C1-Phen/Anth	974.5	283.9	31.2	8.2	692.0	112.5	114.3	144.0	245.9	174.2	75.3	57.7
C2-Phen/Anth	762.6	155.7	96.7	15.4	544.7	53.6	136.2	257.1	129.7	132.5	182.9	81.1
C3-Phen/Anth	318.2	65.9	93.2	12.3	233.2	19.8	101.9	215.6	46.0	59.1	172.0	86.7
C4-Phen/Anth	106.6	31.1	61.7	7.3	75.4	7.9	59.7	165.7	18.7	25.5	119.1	82.4
Dibenzothiophene	90.8	262.4	1.8	1.2	254.3	122.4	54.2	17.1	261.8	69.2	4.9	14.6
C1-Dibenz	177.0	390.5	17.3	6.9	468.0	171.7	72.2	140.8	294.8	56.4	58.6	48.7
C2-Dibenz	210.5	348.5	91.8	22.1	473.0	127.4	106.3	436.3	211.3	73.4	291.0	135.8
C3-Dibenz	140.5	169.9	119.1	22.8	241.8	56.1	97.2	478.5	89.6	51.1	370.9	176.3
Fluoranthene	116.7	71.5	46.4	13.2	41.4	6.2	40.7	28.7	10.9	25.6	31.8	13.7
Pyrene	138.1	33.7	53.0	8.3	29.8	6.7	29.5	39.8	10.8	24.3	36.4	8.2
C1-Fluor/Pyr	248.2	21.4	40.6	5.9	35.8	5.4	27.3	65.4	12.0	28.3	49.7	11.3
Benz(a)anthracene	36.3	5.4	8.8	1.5	2.1	0.6	4.1	10.5	1.2	3.8	6.4	1.2
Chrysene	29.3	25.5	19.7	5.2	11.2	2.7	14.4	22.0	3.7	7.3	29.6	4.4
C1-Chyrsenes	57.2	13.6	17.1	3.2	10.7	1.6	13.4	21.5	3.4	8.6	34.7	4.5
C2-Chrysenes	29.8	16.5	16.4	3.7	13.1	1.9	11.6	11.2	3.1	6.1	33.4	10.2
C3-Chrysenes	5.4	5.8	6.7	0.8	0.8	0.0	3.7	10.0	0.8	1.7	14.2	0.8
C4-Chrysenes	0.9	1.1	29.0	1.3	0.0	0.0	0.5	2.6	0.0	0.0	3.4	1.1
Benzo(b)fluoranthene	18.8	18.8	13.0	5.9	5.9	3.1	10.2	41.0	4.1	8.9	57.1	2.7
Benzo(k)fluoranthene	2.4	2.0	1.6	0.9	0.4	0.4	0.9	2.1	0.6	1.3	6.0	0.6
Benzo(e)pyrene	13.2	7.0	6.4	1.2	2.4	1.3	3.1	15.5	1.9	3.5	9.5	1.4
Benzo(a)pyrene	16.0	2.5	19.0	0.6	0.9	0.6	1.5	11.1	1.1	5.4	34.8	1.2
Perylene	3.3	1.9	4.9	1.0	6.4	0.4	3.5	3.2	1.1	0.7	5.7	0.3
Indeno[1,2,3-cd]pyrene	9.9	2.9	3.3	0.7	1.3	0.6	1.5	1.8	0.9	2.2	3.7	0.8
Dibenz(a,h)anthracene	1.7	0.6	1.3	0.3	0.0	0.0	0.0	0.0	0.0	0.5	1.0	3.3
Benzo(ghi)perylene	17.2	7.9	7.6	0.8	2.2	1.9	2.6	4.2	3.4	5.1	7.9	1.7
2-Methylnaphthalene	1393.3	6406.5	48.7	177.9	9195.6	2004.0	2917.1	129.7	2370.8	2426.4	1383.4	1094.2
1-Methylnaphthalene	1294.4	4643.7	38.4	149.7	8940.6	2460.6	2619.8	121.1	7407.3	7531.9	975.0	962.1
2,6-Dimethylnaphthalene	1975.8	7255.1	42.1	473.1	14682.1	5243.6	4154.4	135.3	10420.4	10234.7	396.6	847.3
1,6,7-Trimethylnaphthalene	792.1	2143.4	28.0	256.6	2994.6	1653.5	828.9	51.6	3347.7	1284.8	96.8	223.8
1-Methylphenanthrene	223.5	77.7	7.9	2.8	139.8	30.0	28.9	38.5	70.0	38.4	20.3	15.5

* FS: fueling station
OT: old oil tank
MS: machine shop
HP: helipad

Table A.5.
Continued.

Sample Identification	Soil 13	Soil 14 MS*	Soil 15	Soil 16	Soil 17	Soil 18	Soil 19	Soil 20	Soil 21	Soil 22	Soil 23
Year	2001	2001	2001	2001	2001	2001	2001	2001	2001	2001	2001
Total PAH	**11,269.6**	**40,618.6**	**703.7**	**663.9**	**1,709.3**	**71,715.9**	**18,946.9**	**19,988.9**	**3,780.4**	**6,691.4**	**722.4**
Naphthalene	281.2	865.3	11.9	6.1	12.9	2813.6	180.4	266.4	67.1	3.6	7.3
C1-Naphthalenes	2454.9	14565.5	55.1	36.3	52.9	24393.3	150.4	3020.8	106.7	16.1	33.9
C2-Naphthalenes	4644.7	15867.4	48.2	29.1	41.3	22712.4	7737.6	7884.8	179.2	16.9	36.8
C3-Naphthalenes	2081.3	4680.2	36.6	17.4	68.4	9050.1	6576.5	5010.6	901.3	43.1	37.9
C4-Naphthalenes	289.0	988.0	32.7	28.0	71.3	1938.2	1673.3	1266.1	944.5	94.1	61.4
Biphenyl	58.3	448.2	4.8	1.7	3.1	3224.0	204.8	400.1	47.9	2.6	3.6
Acenaphthylene	47.3	117.4	0.9	0.9	1.6	509.5	124.5	115.9	23.2	18.7	2.5
Acenaphthene	227.6	100.3	1.3	1.6	2.8	759.9	605.7	423.8	28.2	31.1	10.9
Fluorene	51.4	184.0	3.3	2.1	7.0	857.8	383.6	309.3	31.2	87.2	2.9
C1-Fluorenes	51.1	216.9	89.9	7.4	30.7	842.5	432.9	326.5	72.4	97.4	12.8
C2-Fluorenes	60.2	253.9	25.5	35.9	98.5	604.2	231.4	199.2	144.2	223.3	31.9
C3-Fluorenes	102.9	327.3	70.3	74.0	164.4	428.9	139.1	117.5	183.7	489.4	61.2
Phenanthrene	33.6	136.2	14.5	10.3	21.2	666.2	54.0	72.9	10.8	720.2	7.3
Anthracene	14.5	37.1	1.9	1.2	7.2	234.1	11.9	16.5	9.4	172.5	5.9
C1-Phen/Anth	43.9	137.7	17.2	8.3	78.4	457.4	90.5	105.2	15.3	386.6	7.0
C2-Phen/Anth	74.8	165.2	34.6	31.7	169.1	307.2	61.5	67.4	61.7	398.9	19.3
C3-Phen/Anth	65.1	139.7	31.8	52.6	112.7	179.8	27.8	25.4	79.0	265.6	46.1
C4-Phen/Anth	48.0	167.2	16.4	36.4	66.4	200.6	13.4	11.6	56.4	189.9	42.6
Dibenzothiophene	9.2	55.1	3.0	0.9	1.9	146.8	42.8	63.2	3.2	35.7	1.1
C1-Dibenz	49.0	163.2	10.7	4.8	20.5	136.0	57.2	102.2	14.5	67.3	4.6
C2-Dibenz	155.4	331.0	40.0	50.3	75.9	118.9	53.3	83.6	86.6	141.9	18.7
C3-Dibenz	171.9	269.8	45.9	89.3	78.1	79.2	32.4	41.1	117.8	123.5	58.5
Fluoranthene	57.3	100.5	15.2	25.7	66.8	201.2	7.2	16.5	56.4	1264.6	11.6
Pyrene	45.8	83.8	20.9	22.2	88.3	211.1	7.6	12.8	153.7	789.6	41.6
C1-Fluor/Pyr	23.7	49.6	9.2	17.0	120.8	151.3	11.8	6.8	61.4	227.9	20.8
Benz(a)anthracene	7.5	19.3	3.9	3.5	22.1	84.1	1.1	2.1	18.6	84.1	5.6
Chrysene	24.5	30.6	7.5	12.0	58.2	73.0	4.5	6.1	78.9	282.5	19.0
C1-Chyrsenes	17.1	28.8	8.7	11.2	70.9	48.6	5.4	2.6	32.4	75.1	20.4
C2-Chrysenes	20.0	31.8	13.1	15.9	41.5	44.9	6.2	2.2	23.1	46.2	28.3
C3-Chrysenes	6.8	5.6	2.3	4.8	16.2	9.3	0.0	0.7	0.0	15.4	13.8
C4-Chrysenes	2.3	1.4	0.0	1.5	0.0	0.9	0.0	0.0	4.4	3.5	5.0
Benzo(b)fluoranthene	19.2	15.5	6.1	8.0	5.1	19.5	10.4	3.8	67.5	118.2	14.5
Benzo(k)fluoranthene	4.0	4.3	1.1	1.4	1.2	2.0	1.3	1.0	18.0	22.7	2.6
Benzo(e)pyrene	7.3	9.0	3.2	3.3	2.0	33.0	1.5	1.3	26.2	41.3	6.3
Benzo(a)pyrene	4.8	7.8	2.8	2.5	7.5	73.1	1.0	0.8	11.6	43.0	3.2
Perylene	1.6	2.7	5.2	3.2	3.0	10.4	1.1	0.4	4.7	9.6	4.5
Indeno[1,2,3-cd]pyrene	4.0	4.1	2.7	2.1	6.8	40.9	0.7	0.8	17.8	20.8	3.7
Dibenz(a,h)anthracene	1.2	1.0	1.1	0.2	1.5	6.8	0.3	0.2	3.6	4.6	1.3
Benzo(ghi)perylene	7.2	6.8	4.3	2.6	11.4	45.3	1.8	1.0	18.1	16.7	6.0
2-Methylnaphthalene	997.9	7683.6	34.8	20.3	32.4	13669.9	50.9	1284.1	59.2	9.8	21.4
1-Methylnaphthalene	1457.0	6881.9	20.3	16.0	20.5	10723.4	99.5	1736.7	47.5	6.3	12.6
2,6-Dimethylnaphthalene	1865.5	5510.7	23.9	11.4	19.3	11482.8	4127.1	3745.7	82.6	6.7	17.8
1,6,7-Trimethylnaphthalene	372.7	741.1	9.6	3.8	14.0	2000.0	1486.9	1203.4	220.9	14.5	6.6
1-Methylphenanthrene	13.8	39.2	3.9	2.6	18.4	160.3	29.2	30.8	5.4	119.2	1.3

Table A.6.
Stable carbon isotope ratios (‰) of PAHs in marine sediment and soil samples for Chapter VI.

	Sample Identification	A1	A2	A3	B1	B2	B3	C	A	B	C1	C2	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6
	Year	2000	2000	2000	2000	2000	2000	2000	2001	2001	2001	2001	1999	1999	1999	1999	2000	2000
1	**Naphthalene**	-25.72		-30.94	-27.14	-27.09	-26.78	-25.27	-22.85	-24.32	-25.56		-23.68	-24.08	-24.69	-25.87	-23.59	
2	**2-Methylnaphthalene**	-22.17		-30.12	-25.67	-27.29							-23.32	-25.09			-23.26	-22.17
3	**1-Methylnaphthalene**	-27.61			-25.82	-26.99							-24.48	-25.37			-24.89	-23.78
4	**2MN + 1MN**	-26.73	-26.57	-27.26	-25.80	-27.11	-26.18	-26.15		-26.52	-26.43	-17.52	-23.93	-24.87	-25.90	-22.88	-24.12	-23.21
	C1-Naphthalenes	-24.74		-29.21		-28.09	-26.49		-24.18	-24.58	-24.61	-17.52	-23.92	-25.00	-25.18	-25.36	-25.25	-23.16
	C2-Naphthalenes	-24.80		-25.08	-25.80	-24.86	-25.04	-24.12	-24.24	-24.26	-25.31	-22.47	-24.27	-24.46	-24.76	-24.27	-25.60	-23.37
	C3-Naphthalenes	-25.38		-25.20	-22.75	-20.28	-22.81	-25.61	-23.88	-23.86	-24.76	-26.01	-23.67	-22.08	-25.49	-25.16	-23.57	-22.46
5	**Biphenyl**				-25.60	-22.90	-25.18	-23.66			-26.12						-23.63	
6	**2,6-Dimethylnaphthalene**	-23.10		-25.39	-22.76	-22.58	-23.13	-23.56		-22.49	-23.64		-23.72	-22.12		-22.32	-22.84	-23.09
7	**Acenaphthylene**			-28.59	-20.25	-17.15	-25.38	-11.05			-18.91		-24.96				-22.91	-24.15
8	**Acenaphthene**	-24.66			-25.12	-26.32	-24.78	-27.26	-22.11	-21.75	-18.59	-29.34		-22.88		-22.66	-23.14	
9	**1,6,7-Trimethylnaphthalene**	-25.52		-22.19	-21.18	-14.23	-20.87	-25.91	-18.28	-18.35	-21.60		-22.66	-23.27			-23.03	
10	**Fluorene**	-22.82		-22.61	-24.35	-24.22	-24.69	-34.51			-21.15		-20.99	-22.18		-22.43	-22.71	
	Dibenzothiophene	-17.23		-20.98	-26.04	-26.40	-23.73				-20.07							
11	**Phenanthrene**	-21.93			-23.89	-20.26							-23.83				-22.53	
13	**Phe + Ant**	-22.24	-22.41	-23.76	-23.81	-17.64	-23.75	-23.64	-22.51	-21.03	-23.44	-23.25	-24.33	-21.56		-23.22	-26.07	
14	**1-Methylphenanthrene**	-20.95	-19.84	-21.24	-24.44		-23.13	-23.23	-20.51	-25.43	-23.54	-22.81	-25.08	-21.31			-22.94	-24.76
	C1-Phenanthrenes			-20.31	-24.15	-23.66	-23.57	-25.80			-23.04	-23.26	-25.31	-22.86			-24.99	
15	**Fluoranthene**	-24.10	-23.18	-23.40	-23.89	-24.64	-23.85	-24.10	-21.33	-25.72	-23.46	-24.18	-23.05	-23.07	-25.66	-22.78		-22.48
16	**Pyrene**	-24.27	-23.13	-23.47	-23.53	-22.24	-23.55	-23.52	-23.27	-23.86	-23.99	-23.65	-23.57	-24.67	-26.47	-24.25	-22.34	-22.58
19	**BaA + Chr**	-22.93	-23.29	-23.85	-23.91	-19.72	-24.53	-26.50	-24.69	-28.87	-23.64	-23.79	-24.70	-24.40	-26.24			
22	**Benzo[b+k]fluoranthenes**	-24.45	-23.71	-24.89	-24.70	-24.64	-25.35	-24.82	-22.72	-26.29	-23.61	-23.83	-24.03	-25.51	-26.87		-20.85	
26	**BeP + BaP + Per**	-24.75	-20.30	-23.62	-25.95	-25.42	-22.69	-24.60	-18.94	-25.16	-23.97	-25.26	-20.13	-24.83				
29	**INP + DBA**	-23.47	-21.70	-20.55	-26.78	-26.00	-26.56				-26.21	-23.92	-23.38	-25.72				
30	**Benzo[ghi]perylene**	-26.74	-24.04	-23.56	-23.80	-23.67	-28.22			-26.42	-24.99	-24.25	-23.55	-26.89				

Table A.6.
Continued.

	Sample Identification Year	Soil 7 2000	Soil 8 2000	Soil 9 2001	Soil 10 2001	Soil11 2001	Soil 12 2001	Soil 13 2001	Soil 14 2001	Soil 15 2001	Soil 16 2001	Soil 17 2001	Soil 18 2001	Soil 19 2001	Soil 20 2001	Soil 21 2001	Soil22 2001	Soil 23 2001
1	**Naphthalene**	-21.63	-25.10	-24.30	-23.76	-23.96	-25.09	-21.29	-25.85			-17.64	-25.86		-25.51	-24.80		-25.47
2	**2-Methylnaphthalene**	-22.82	-24.31		-24.29	-23.92	-22.85		-26.03			-28.35	-27.45		-24.20			
3	**1-Methylnaphthalene**	-24.37	-25.08		-25.53	-24.61	-24.93		-26.89			-28.75	-25.30		-24.98			
4	**2MN + 1MN**	-23.66	-25.02	-24.67	-24.08	-24.24	-24.70	-23.99	-26.29	-27.51		-27.57	-26.80	-23.37	-24.66	-24.12		-27.37
	C1-Naphthalenes		-24.34	-24.44	-24.32		-25.64	-23.79	-23.38				-26.20	-23.65	-24.73	-24.42		-28.84
	C2-Naphthalenes	-23.93	-24.75	-25.56	-25.20	-23.57	-24.47	-24.80	-25.57	-27.58	-25.56	-25.54	-27.31	-23.76	-26.26	-27.37		-24.44
	C3-Naphthalenes	-23.53	-23.36	-23.23	-24.01	-23.07	-23.98	-23.37	-23.82			-23.21	-26.53	-23.73	-24.57	-25.40		
5	**Biphenyl**	-23.60										-26.13	-25.20		-23.85	-22.70		
6	**2,6-Dimethylnaphthalene**	-23.73			-22.88	-19.32	-22.75	-24.10					-26.52	-22.17	-24.27	-26.64		
7	**Acenaphthylene**	-24.99			-23.20	-18.69		-25.33				-20.36	-27.61		-24.64	-21.11		
8	**Acenaphthene**	-23.71		-22.85	-22.96	-22.63	-23.21						-27.09	-22.64	-25.10		-23.61	
9	**1,6,7-Trimethylnaphthalene**			-22.16	-19.32					-21.42	-17.47	-21.16	-24.60	-22.72	-24.49	-22.11		
10	**Fluorene**	-22.82		-26.33	-23.12		-21.82			-24.26	-22.49	-21.58	-26.87	-28.28	-21.65	-21.75	-22.60	
	Dibenzothiophene						-20.95			-7.27	-12.11	-20.65					-24.39	
11	**Phenanthrene**									-23.99	-28.14	-23.28						
13	**Phe + Ant**	-25.80	-25.99				-25.80		-27.71	-24.69	-20.50	-23.31	-24.00				-24.47	
14	**1-Methylphenanthrene**	-25.12		-24.50	-25.91			-19.46		-24.33		-23.09	-27.27	-21.93	-24.75	-20.87	-24.45	
	C1-Phenanthrenes						-25.65			-22.75	-20.06	-25.53	-30.78		-22.96	-25.65	-24.15	
15	**Fluoranthene**	-20.95			-21.65	-20.30	-22.20	-25.33	-24.09	-21.97	-23.75	-25.59	-25.22	-20.88	-21.29	-24.25	-24.58	-24.67
16	**Pyrene**	-21.81	-23.42		-23.68		-25.44	-24.59	-24.75	-18.12	-24.04	-25.42	-28.37	-24.88	-24.24	-22.89	-24.85	-32.34
19	**BaA + Chr**				-24.19			-26.48	-26.70	-25.64	-24.25	-31.80		-32.77	-23.04	-26.11	-24.33	
22	**Benzo[b+k]fluoranthenes**	-23.73						-25.17		-27.59	-21.64	-32.13	-25.06	-22.77	-26.01	-17.90	-24.83	
26	**BeP + BaP + Per**									-18.55	-24.37	-24.83	-26.57			-30.32	-25.02	
29	**INP + DBA**							-33.39					-18.63			-25.36	-25.30	
30	**Benzo[ghi]perylene**	-22.49					-23.67	-19.16					-25.05			-26.79	-26.56	

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